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INVESTIGATION OF THE COPRECIPITATION OF SULFIDES BY MEANS OF RADIOACTIVE INDICATORS

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The coprecipitation of various substances which, under the experimental conditions, should remain in solution, with analytical precipitates of low solubility is very common in chemical analysis.

Coprecipitation interferes with the preparation of pure precipitates of the correct stoichiometric composition, and also with complete separation of the elements, where it plays a negative part. This phenomenon has real significance, since it presents a possibility of separating traces of elements and also of studying the properties of elements at very high dilution.

The laws governing the processes of trapping easily-soluble compounds by a solid phase at the moment of their separation or formation have been studied by macro-, micro- and ultramicro- quantitative methods. In experiments on coprecipitation on the macro and micro-scales, normal analytical methods are used. When working on the ultramicro scale, where dilution can be of the order of 10^{-20} mol/liter, the methods already indicated are not suitable. In order to investigate the properties of such small amounts of material, radiochemical methods are employed, which have the considerable advantage over normal chemical methods that they enable the properties of the substance to be studied on an unweighable amount. The sensitivity of radiochemical methods is very high. By measuring the radiation it is possible to study the behavior of 10^3 to 10^4 atoms.

Of particular significance in the study of coprecipitation is the radiographic method, which enables the nature of the distribution of the substance in the solid phase to be made clear.

In carrying out coprecipitation reactions the state of those microquantities of substances which we wish to separate together with the solid phase is a very essential factor. Coprecipitation proceeds differently according to the degree of dispersion. If as a result of supersaturation or the formation of colloidal solutions the precipitate does not separate, this can be effected by precipitating it together with some other precipitate in the given solution.

Substances present in ultra-micro amounts behave similarily when the solubility product is not reached even for the most insoluble compounds, such as certain hydroxides and sulfides.

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1) L.I.Guseva and V.F.Leonov participated in this work.

If the substance is in solution in negligibly low concentration, as would be the case, e.g., with radioisotopes, then in accordance with their nature the aqueous solutions will either be true or colloidal solutions. Radioisotopes are present in amounts which are not sufficient for the formation of particles of colloid size.

The capacity of radioisotopes to be trapped with a precipitate will differ according to whether they are in the form of radio colloids, molecules, or ions. The formation of radio colloids is determined by the low solubility of the respective components and their tendency to hydrolyze. The capacity of elements under given conditions to form an easily soluble complex compound will eliminate the formation of radio colloids. Since the concentrations of radio isotopes are very small, then in "trace chemistry", , adsorption plays an important role, particularly if the substance is in the form of a radio colloid.

Characteristics of the Properties and Composition of Sulfides

Heavy metal sulfides are the least soluble class of compounds used in analytical chemistry. By means of H_2S, the metals of the second and third analytical groups can be readily separated from many other metals, and traces of metals separated.

The concentration of acid in solution plays a very important part in the formation of sulfides. Such compounds as Bi_2S_3, PbS and CuS do not precipitate completely if the acid concentration is increased. As_2S_5, GeS_2, Re_2S_7, on the other hand, can only be precipitated at high values of the hydrogen ion concentration. This can be explained by the fact that As(IV), Ge(IV) and Re(VII) are in solution in the form of anions of the hydrogen acid or as undissociated weak acids. At high hydrogen ion concentrations it is natural to assume the presence of H_3S^+ cations which react with the anions of the acids indicated. Under these conditions HS^- and S_2^- ions do not play an essential part.

The structure (crystalline or amorphous) of the sulfides plays an important part in their precipitation, as well as the morphological form of the precipitate (powdery, flocculent, or gel-like), which depends on the conditions of formation and ageing. Considerable changes in the physical and chemical properties of the sulfides occur during ageing.

As examples we may adduce the α, β, γ forms of NiS which are obtained under different conditions and which differ from each other in structure and solubility. Cobalt sulfide also apparently exists in various crystalline forms which differ in their solubility.

There are two modifications for ZnS – α and β: the α separates from acid media while the β-form precipitates from alkaline media. The α-ZnS form differs from the β-form by a lower solubility in acid media, containing H_2S. Antimony sulfide (III) can also be obtained in different forms according to the method of precipitation. The forms which differ from each other most are the orange-red form, which is bulky and friable, and the black crystalline form, which has a higher density. The first of these forms of Sb_2S_3 is obtained under normal conditions, while the second is precipitated from strong HCl solutions. It is of interest to note that the black crystalline modification of Sb_2S_3 is purer than the orange one. The Sb_2S_3 which precipitates from HCl solution also contains the chloride which cannot be removed by washing.

Black mercuric sulfide is labile; it crystallizes in the normal system. On ageing, HgS is transformed into the stable modification with a red color and with a hexagonal crystalline form. The rate of transition from one form into the other depends on the acid concentration, temperature, and H_2S concentration.

One of the characteristics of the sulfides is the variability of the composition of the precipitates formed, even when only one sulfide is concerned. Sulfides such as HgS, CdS and PbS during their formation give compounds which differ in composition from the normal sulfides. On precipitating Hg in the presence of large amounts of HCl a compound of the composition $Hg_3S_2Cl_2(2HgS\cdot HgCl_2)$ is formed. This intermediate compound is also formed in sulfuric acid solutions of $HgCl_2$. However, on passing H_2S into a sulfuric acid solution of mercuric perchlorate, the above compound is not formed.

When cadmium is precipitated in the form of the sulfide from HCl solution, a precipitate is formed just as in sulfuric acid solution, which does not correspond to the formula CdS, but in addition contains cadmium chloride when precipitated from HCl solution and cadmium sulfate when precipitated from H_2SO_4 solution. The composition of the precipitates depends on the precipitation conditions. The effect of these characteristics of the sulfides has not been studied sufficiently; meanwhile, they are of great significance in the phenomenon of coprecipitation of these compounds.

Conditions for the Formation of Sulfides

The amount of various metals which is precipitated with the sulfides depends to a large extent on the conditions under which they are formed and on further changes during ageing.

Since the sulfides are only very slightly soluble, the rate of formation of their nuclei is large; the nuclei do not grow but give rise to a sol which coagulates after being formed. As a result of adsorption of S^{2-} and HS^- the sol has a negative charge. On coagulation of this kind of sol the cations are trapped by the precipitate. The number of cations trapped by the sulfide of a given metal depends on the dispersion of the sol and the charge of the cation.

The tendency of metals to coprecipitate is determined by the solubility of their sulfides and by other factors: isomorphism, the formation of chemical compounds, adsorption, etc..

Trapping by metal sulfides varies in accordance with precipitation conditions (H_2S concentration, rate and length of time for which the H_2S is bubbled through the solution). When H_2S water is used the amount of coprecipitation will depend on whether the initial salt is added to the solution or vice versa.

A rapid flow of H_2S for a long time yields precipitates with a large adsorbing surface. The effect of the H_2S concentration on the order of addition of the solutions during precipitation of sulfides by means of H_2S water on the precipitate is similar.

Apparently coprecipitation of metals with sulfides will be least when the crystalline structure of these compounds will be most clearly expressed. Separation of sulfides in a crystalline form can be achieved by slowing down the process of their formation.

Ostroumov and Maslennikova [1] prepared NiS and CoS in a crystalline form by precipitation in the presence of pyridine.

Sulfides can be precipitated by means of ammonium thiocarbamate [2].

Trapping of cations from solution by the sulfides continues after separation of the solid phase, and therefore the ageing of these precipitates affects the process considerably. Ageing, which is an important factor in the case of the sulfides, is related to a number of physico-chemical changes in these compounds, viz., changing over from an amorphous to a crypto-crystalline form, and change in the degree of aggregation and hydration. When sulfides which contain a large amount of water are dehydrated, their specific volumes change considerably.

From what has been said it follows that when studying the coprecipitation of metals with sulfides, each individual factor in the precipitation, though at first sight of little significance, should be carefully taken into consideration.

The Coprecipitation of Metals With Sulfides

The trapping of other ions from solution by precipitates was discovered long ago. It should be noted in this connection that a great deal of attention has been given to this phenomenon by Russian chemists, but nothing has been said in the literature till recently.

Even as long ago as 1886 the coprecipitation of considerable amounts of iron with sulfides of the platinum metals was observed by Vilm [3] while analyzing platinum ores.

A large number of investigations was subsequently devoted to a study of the precipitation of macro amounts of metals with sulfides. These experiments were the subject of disputes, both with regard to the possibility of preparing pure precipitates of these compounds during coprecipitation, and the reasons for coprecipitation.

In the opinion of N.A.Tananaev [4], during the precipitation of Cd and Hg or Zn and Cu by H_2S, formation is possible of compounds of the type of the sulfosalts - $CdHgS_2$ or $ZnCuS_2$, which are otherwise more soluble in acids than the sulfide compounds forming the given sulfo salt (analogous to Na_2HgS_2, which is soluble in water).

A number of investigations were carried out by Kolthoff and coworkers [5-9] on the trapping of metals of the third analytical group by sulfides of the second group. They consider that this phenomenon is the consequence of the subsequent precipitation which occurs as a result of the adsorption of H_2S on the sulfides of the H_2S group, which causes precipitation of the metals of the third groups.

In Fiegl's opinion [10] coprecipitation of metals of the third group with metals of the H_2S group occurs because of the subsidiary valency forces of sulfur. As the author points out, as a result of coprecipitation the following coordination compounds can be formed: a) hydrosulfides $MeS - SH_2$; b) polysulfides $MeS - S$; c) isopolymers $MeS - SMe$; d) heteropolymers $MeS - SMe_2$.

In connection with Fiegl's work it is of interest to note that in a paper published fairly recently by Fialkov and Muzyka [11] they reported the formation of polysulfides of the following composition: ZnS_4, ZnS_3, ZnS_2, CdS_3, CdS_4 and CdS_5, as a result of the interaction of salts of Cd and Zn with $(NH_4)_2S_2$ and $(NH_4)_2S_5$.

Ruffu and Hirsch [12] during their work on the fractional separation of metals also investigated the coprecipitation of metals of the third analytical group with the sulfides of the second. In their opinion, during the fractional separation of metals, the law of mass action and the solubility product are decisive factors. The formation of mixed crystals, occlusions, and adsorption are of little significance, according to them.

Balarev [13] reckons that the trapping of Zn by CuS is caused by internal adsorption of the zinc by the capillaries present in the particles of CuS.

The coprecipitation of micro amounts of various metals with the sulfides has found wide application for their separation and concentration. Chuiko [14] has carried out some systematic work along these lines. This author separated microgram quantities of copper with the following sulfides: CdS, PbS and SnS.

Gulyaeva and Itkina [15] separated small amounts of copper in the presence and in the absence of cadmium salts. The separation of copper on lead sulfide has also been adopted by many authors [16].

Molybdenum sulfide, which is difficult to precipitate, has been separated with CuS [17].

In addition, investigations have been made on the separation of small amounts of copper on the sulfides of Cd, Pb, and Sn [18].

The coprecipitation of ultra micro amounts of metals with sulfides has been used for the study of the properties of substances at extreme dilutions, and also for the separation and purification of the radio isotopes of various metals.

Thus, during a study of the radio isotope Pb^{212}, it was separated by means of ammonium sulfide with Bi_2S_3 [19].

A similar investigation was carried out with Bi^{210} during its precipitation with PbS [20].

Bi_2S_3 [21] was used for a study of the relation between the capacity of Pb^{212} to precipitate and the solubility of lead salts.

This radio isotope of lead was also separated on Ag_2S prepared beforehand [22].

Pa^{231} was precipitated with Bi_2S_3 and PbS by means of $(NH_4)_2S$, and was separated from tin [23] in this way.

This radio isotope was separated with H_2S from acid media on the following sulfides: CuS, Sb_2S_3, HgS, and Bi_2S_3 [24].

In the course of a study of the coprecipitation of Th^{234} with FeS in the presence of $(NH_4)_2CO_3NH_4Cl$ [25] by means of $(NH_4)_2S$, it appeared that the FeS was inactive.

The properties of At^{211} were investigated by separating it with HgS from HCl media by means of H_2S [26].

Traces of Tc^{96} were coprecipitated from HCl media with PtS and Re_2S_7[27], and also with CuS and MnS [28].

A considerable amount of work has been devoted to investigations of the coprecipitation of metals and sulfides. On the basis of these investigations, however, it can be concluded that in the strict sense of the word there is no theory of coprecipitation for a given class of compounds.

The question of the trapping of metals by sulfides has been solved by various authors in the course of investigations which have not been carried out under identical experimental conditions, as a result of which different explanations are put forward for the coprecipitation of one and the same metal with the sulfides. Moreover, these investigations have only been carried out with a limited number of metals, and only limited application of physico-chemical methods of analysis.

An explanation of the nature of coprecipitation, apart from its theoretical importance, is also extremely important for analytical chemical practice, since a knowledge of the sources of errors enables us to avoid them and to get practically pure analytical precipitates. Moreover, in this way it becomes possible to use H_2S for exact quantitative separation.

It is therefore desirable to start systematic investigations on the trapping of various metals by sulfides, in which the greatest possible number of combinations of precipitated metal-metal sulfide is considered, so that a general relation may be deduced.

It is essential that particular attention be given to a study of the conditions under which the sulfides are formed. A study of the coprecipitation of sulfides is necessary, both for the separation of metals of the H_2S group from sulfides of the third group, and also for the study of the trapping of metals by sulfides, particularly in cases where we are dealing with very small amounts.

Special attention should be given to radio-chemical methods, which have exceptional possibilities in this field.

The present work is the first part of work done along these directions, in which results on the coprecipitation of Zn, Co, and Fe with the sulfides of the H_2S group are adduced.

EXPERIMENTAL

Salt Solutions Used

In order to carry out these investigations, 0.1 M solutions of the chlorides of Hg(II), Bi, Cd, Cu, Sb(III), Sn(II), Sn(IV), and of $AgNO_3$ and 0.02 M $PbCl_2$ were prepared. In experiments with arsenic a 0.1 M solution of sodium arsenite was used. Solutions of Zn, Co, and Fe(III) were also 0.1 M solutions of the chlorides of these metals. The solutions were standardized either gravimetrically or volumetrically. Copper was separated electrolytically. Chemically pure grades of the salts of the metals indicated above were used.

Precipitation of the Sulfides and Determination of the Amounts of Zn, Co, and Fe Trapped

During an investigation of the phenomenon of coprecipitation it is essential that all the conditions which can affect the amount of trapping of various impurities by the precipitate to some degree of another, should be carefully observed in order that reproducible results can be obtained. It is necessary, however, to observe that very often, even when all the conditions are reproduced exactly, the amount of material trapped can vary considerably in parallel tests. This becomes comprehensible if it is borne in mind that the process of formation of the solid phase, starting from the moment when the first nuclei appear to the appearance of the first opalescence, can take place at different rates. That this is so is indicated by the fact that it is necessary to add various amounts of precipitant in order to get the first appearance of turbidity. When coprecipitation is very marked, the amount of substance trapped in parallel tests shows variations which are well outside the limits of the accuracy of the gravimetric determinations.

The following factors were taken into consideration when choosing the precipitation conditions for the metals tested: rate at which H_2S is bubbled through the solution, temperature, acid concentration, and the time of standing of the solution plus solid phase before filtration. The experimental conditions just enumerated are essential factors in determining the structure, dispersion and composition of the precipitates, and thereby affect the extent of coprecipitation.

The application of radio isotopes for determining the amount of element coprecipitated has considerable advantages over the ordinary chemical methods. "Labelled" atoms enable the amount of coprecipitated metal to be determined directly from the activity of the precipitate. Thus the work is considerably simplified. The determination of metals on the precipitates of various sulfides is often a difficult problem, particularly if the given metal is present in small amounts.

It is essential, however, to note that in order to get correct results the radio isotopes used must be thoroughly purified themselves, so that it is possible to speak of radiochemical purity. In addition a number of blank tests must be carried out, in which various factors which can affect the accuracy of the determination are taken into account, e.g., such factors as the screening action of the precipitate (particularly when using soft radiation); adsorption of the radio isotope by the filter; and the geometrical conditions used in measuring the activity.

Two series of experiments were carried out, in which ca. 10 mg and 100-200 mg lots of sulfides were precipitated, respectively. In the first case the amounts of Zn, Co and Fe were small, while in the second case they were present in equimolar amounts.

The experiments with the small amounts were carried out as follows: To a 25 ml flask were added 0.1 m-mole of the solution of the metal of the fourth or fifth group, 0.5 ml of a solution of the radio isotope, and HCl added until its final strength was 0.3 N[1], and the contents of the flask made up to 25 ml with distilled water. H_2S was passed through the solution after being preliminarily passed through a wash bottle containing water. The H_2S rate was 50-60 bubbles per minute, the temperature of the solution being 18-20°. Filtration was carried out under pressure 18 hours after precipitation, through a close grained filter 3.5 cm in diameter and with a 6-7 mm edge. The filter was placed in a funnel with a porous plate. The precipitate was washed 8-10 times with 3 ml of a 0.1% ammonium chloride solution saturated with H_2S.

After drying the filters were placed in tracing cloth envelopes, and their activities determined. The activity of 0.5 ml of a solution of the respective radio isotope placed on a filter and prepared in the same way was measured in parallel. The amount of radio isotope adsorbed by the filter under our experimental conditions and the screening activity of the sulfide precipitates were determined in separate experiments. The percentage coprecipitation was then determined from these results.

The labelled atoms used were the following radio isotopes: Zn^{65}, Co^{60}, and Fe^{59}. They were carefully purified before use. The solutions of $Zn{\cdot}Cl_2$, $Co{\cdot}Cl_2$ and $Fe{\cdot}Cl_3$ were used in amounts corresponding to the following ratios in the precipitation solution: Zn^{2+}: Me^{2+}, Me^{3+} = 1:12; Co^{2+} : Me^{2+}, Me^{3+} = 1: 5,000; and Fe^{3+} : Me^{2+}, Me^{3+} = 1.6:10.

The radioisotopes were purified as follows: Zn and Co were reprecipitated several times, while the ferric chloride was purified by repeated extraction with ethyl ether. In the case of zinc the reaction selected for purification was precipitation in the presence of iron salts with alkali, and subsequent separation as the sulfide at a pH of 2-3. Cobalt was purified by precipitation in the form of potassium cobaltinitrite and α-nitroso-β-naphthol.

The 0.5 ml of a solution of the radio isotope indicated gave ca. 15,000 impulses/minute. Preparations with low activity were measured for 20-30 minutes.

The relative error of measurement was calculated from the formula

$$\delta' = \frac{\delta E}{E} = \frac{0.67}{E} \sqrt{\frac{E+\Phi}{t_1} + \frac{\Phi}{t_2}}$$

where δ' is the relative error of the result, δE the error of measurement, E the number of impulses per unit time, t_1 the time during which the activity of a preparation was measured, t_2 background, and Φ the number of impulses of the background.

Calculation shows that in this way it is possible to determine 0.1% of the metals indicated above (see Table 1).

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[1] In experiments with Ag_2S precipitation was effected from 0.3 N HNO_3.

In experiments with large amounts of sulfides the precipitation was carried out from 100 ml, the H_2S being bubbled through for 15 minutes. 10 ml of 0.1 M solutions of the respective metals of the H_2S group and 10 ml of 0.1 M $ZnCl_2$, $CoCl_2$, and $FeCl_3$, respectively, were used for precipitation. The amount of Zn, Co and Fe trapped was determined from the amount left unprecipitated, either gravimetrically or volumetrically.

In the remaining cases the experiments were carried out in a similar way with small amounts of sulfides.

TABLE 1

Coprecipitation of small amounts of zinc, cobalt, and iron with the sulfides of the metals of the H_2S group

No.	Metal sulfide	Found in the ppt. in %		
		Zn	Co	Fe
1	HgS.......	0.8	3.2	0.14
2	CuS.......	0.7	0.11	0.10
3	CdS.......	7	0.10	0.19
4	Bi_2S_3.....	0.4	0.10	0.15
5	SnS_2......	10	17.20	1.81
6	SnS.......	–	2.20	0.50
7	Sb_2S_3.....	0.3	0.12	0.15
8	As_2S_3.....	0.4	<0.10	0.16
9	PbS.......	0.3	<0.10	0.15
10	Ag_2S......	0.2	<0.10	0.10

TABLE 2

Coprecipitation of equimolar amounts of zinc, cobalt, and iron with the sulfides of the metals of the H_2S group

No.	Metal sulfide	Found in the ppt. in %		
		Zn	Co	Fe
1	HgS......	40.2	5.5	<0.3
2	CuS......	11.2	0.5	2.4
3	CdS......	9.5	3.4	3.2
4	Bi_2S_3....	3.7	2.5	0.5
5	SnS_2.....	3.0	8.1	8.9
6	SnS......	1.9	1.5	2.0
7	Sb_2S_3....	1.5	2.1	6.5
8	As_2S_3....	1.1	1.0	2.8
9	PbS......	0.5	1.1	1.6
10	Ag_2S.....	<0.3	<0.3	<0.3

The results, which are adduced in Table 1, show that the amount of Co and Fe trapped by almost all the sulfides of the fourth and fifth groups is very small. The exception is SnS_2, with which a considerable amount of Co is precipitated.

The amount of Co precipitated with HgS and of Fe with SnS_2 is fairly high. Considerably more Zn is trapped in the precipitate as compared with Co and Fe. According to these results the coprecipitation of Zn with CdS and SnS_2 is especially marked.

It is interesting to mention some of the observations made during these experiments, the results of which are given in Tables 1 and 2.

After precipitation of the sulfides, a clear cut difference was observed in the volume occupied by a given precipitate. The outstanding precipitate was Sb_2S_3, which had the greatest volume. The sulfides of Hg (II), Pb, Ag, and Cd, on the other hand, had the least volume of all the sulfides; the volume of these sulfides was several times less than that of Sb_2S_3. The volumes of the precipitates of the other sulfides were intermediate between the volumes of the four sulfides mentioned above and that of Sb_2S_3.

Filtration of the sulfides was satisfactory, with the exception of SnS_2. The SnS_2 precipitated in the presence of Co had a brownish yellow color, and not the usual yellow color. In this case coprecipitation is much more marked as compared with the other sulfides.

Discussion of Results

The general conclusion which follows from a comparison of Tables 1 and 2 is that the amounts of Zn, Co, and Fe trapped by the precipitate for small amounts of Zn, Co, and Fe are considerably less than when large amounts of these three elements are present. The behavior of Co during the precipitation of SnS_2 (see

Experiment 5, Tables 1 and 2) is of interest in this connection, for small amounts of Co the amount of coprecipitation is considerably greater than when large amounts of Co are present.

The results in Table 2 show that when Zn, Co, and Fe are present during the precipitation of the H_2S group of elements, coprecipitation varies for any given metal of this group. Thus, those conditions which are usually recommended in analytical textbooks, i.e., precipitation from a solution 0.3 N with respect to acid, do not lead to a complete separation of these metals. Coprecipitation is particularly marked in the case of Zn and HgS, where it amounts to 40%.

It is of interest to note that Co and Fe coprecipitate with SnS_2 in large amounts, while the extent of coprecipitation with SnS is low. This is probably the result of oxidation of Sn from the bivalent to the quadrivalent stage. On comparing the crystalline lattices of SnS_2 and SnS it appears that SnS has a rhombic lattice, while SnS_2 has a hexagonal one. The sulfides of Co and Fe also have a hexagonal lattice. This apparently also explains the large difference between the coprecipitation of the two metals with SnS_2 and SnS.

A similar phenomenon can be observed in the coprecipitation of Zn with HgS. Both the HgS and ZnS have a cubic lattice. It should be borne in mind that HgS immediately after precipitation has a hexagonal lattice, but this subsequently changes into a modification having a cubic lattice.

The fact that, as a rule, in our experiments coprecipitation occurs to a lesser extent for small amounts of Zn, Co, and Fe is of interest. In this connection, therefore, the question arises as to why, in the experiments with Sn(IV) for small amounts of Co, does coprecipitation increase considerably. An explanation of this fact may be sought in an increase in the relative adsorption with decreasing concentration of the trapped ion.

Investigation of the coprecipitation of sulfides continues. It is necessary to point out that in order to make a deeper study of this phenomenon it is essential that such methods as radiography, electron microscopy, and X-ray spectrography be used, whereby the relations between coprecipitation and structure, dispersion, and the conditions of formation of a given sulfide can be established.

In addition, special attention must be given to a study of the actual process of formation of the sulfides, using photographic methods for this purpose.

In conclusion I should like to express my thanks to Prof. I.P. Alimarin for directing the work.

SUMMARY

1. During the precipitation of 10^{-3} mols of HgS, PbS, SnS_2, SnS, CdS, CuS, and $0.5 \cdot 10^{-3}$ mols of Bi_2S_3, As_2S_3, Sb_2S_3 from 0.3 N HCl and of Ag_2S from 0.3 N HNO_3 in the presence of equimolar amounts of $ZnCl_2$, $CoCl_2$, and $FeCl_3$, coprecipitation of these metals occurs.

2. Coprecipitation was most marked for the following metals: Zn with HgS (40.2%); CuS (11.2%); CdS 9.5%; Bi_2S_3 3.7%; SnS_2 3%; Co with SnS_2 8.1%; HgS 5.5%; CdS 3.4% and Fe with SnS_2 8.9%; Sb_2S_3 6.5%; CdS 3.2%; As_2S_3 2.8%.

3. Coprecipitation is least for Zn, Co, and Fe with Ag_2S ($<0.3\%$). Coprecipitation varied in the remaining cases from 0.5-2%.

4. During precipitation of the sulfides indicated above in amounts of $0.5 \cdot 10^{-4}$-10^{-4} mols in the presence of small amounts of Co and Fe, the amount of coprecipitation observed for these metals was insignificant (0.1-0.2%), with the exception of SnS_2 and HgS. The coprecipitation of Co with SnS_2 amounts to 17.2%, of Fe 1.81%, and for Co with HgS to 3.2%.

Zn is trapped to a far greater extent than Co and Fe, particularly with CdS 7% and with SnS_2 10%.

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THE ULTRA-MICRO METHOD OF CHEMICAL ANALYSIS

COMMUNICATION 2

THE ELECTROLYTIC SEPARATION AND DETECTION OF METALS

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By using the apparatus for ultra-microchemical determinations and the corresponding auxiliary apparatus [1,2], it is possible to examine small volumes of solutions (10^{-3} - 10^{-4} ml) by means of various analytical methods.

The apparatus and experimental technique for analysis by ultra-micro methods have a specific character. The procedures adopted for the simplest chemical operations (filling flasks with liquids, pouring from one to the other, measuring the requisite volumes, precipitations, etc..) and the apparatus necessary for these procedures, have been adequately described [2]. However, in order to carry out a qualitative analysis of some object or other, more diverse forms of apparatus are necessary, as well as a greater number of operations.

The electrolytic deposition of metals from solution is an excellent method for separating and detecting the elements. By means of special apparatus and the respective techniques, electrolysis can be carried out using the microscope both with solid [3,4] and with liquid electrodes. It should be noted, however, that the application of electrochemical methods to the ultra-micro analysis of inorganic compounds has not yet been described.

The question of what is the minimum amount of a metal which it is necessary to have in solution in order to deposit it electrolytically can be solved by means of Nernst's equation. A calculation for the case of copper ions gives the following results: the deposition potential of copper from a normal solution is 0.34 V. In view of the fact that the hydrogen overvoltage on copper is 0.23 V, then the potential of the cathode can be adjusted to this value. At such a potential the copper ion concentration in solution will be given by:

$$-0.23 = 0.34 - \frac{0.058}{2} \log \frac{1}{c}; \quad 0.57 = 0.029 \log \frac{1}{c} ,$$

from which $c = 10^{-20}$. This concentration is outside the limits of any qualitative determination.

In order to deposit any element electrolytically certain conditions must be observed. The potential during electrolysis even in the ultra-micro method must naturally in any case be not less than the decomposition potential of the electrolyte. As a result of the small surface of the electrodes used in ultra-micro methods, the necessity of observing a definite value for the current density (0.1 - 0.01 A/cm^2) means using a current density of $10^{-4} \div 10^{-5}$ A.

Electrolysis With Platinum Microelectrodes

Platinum electrodes possess the advantage that they exclude the possibility of contamination of the solution with foreign ions during electrolysis. In ultramicro methods, therefore, they are given preference to solid electrodes made from any other metals.

a) Apparatus

The electrolytic deposition of metals from small volumes of the order of $1\lambda (10^{-3}$ ml) can be effected by using special micro apparatus which differs from the apparatus used for macro electrolysis in that part of the apparatus where electrolysis actually occurs. The electrical set up is left practically unchanged; the current flows from an accumulator (a 4-6 volt source of D.C.), through a switch resistance box into an electrolytic micro cell.

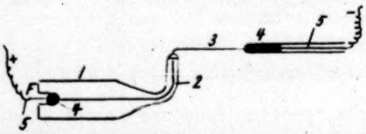

Fig. 1. Electrolysis on a condenser rod.

1 - condenser rod; 2,3 - electrodes; 4 - mercury contacts; 5 - current leads.

Electrolysis using platinum micro electrodes can be carried out by two methods:

1. The test solution is placed on the end surface of a thick walled capillary (external diameter ca. 5 mm, internal diameter 0.5 mm) in the form of a condenser rod [2] (Fig. 1), into the bore of which has been fused a platinum wire of diameter ca. 0.1 mm, one end of which finishes up in the end surface of the condenser rod and serves as the anode. The other end of this wire is located inside the capillary at some distance from its other end; mercury is introduced into the bore of the capillary from this side so that the anode is in contact with the lead-in for the current. The cathode is also a platinum wire fused into an ordinary capillary (Fig. 1) so that one end sticks out of the capillary, while the other is located inside the capillary. A small drop of mercury is placed on the capillary so that contact is established between the cathode and the lead-in for the current. The end which sticks out is bent at right angles over a small length of the wire and serves as the cathode. The capillary is mounted in a glass tube. When an electrolytic cell of this kind is used, a humidity cabinet of a different design to that described previously is required [1,2]. The brass walls of the cabinet are not unbroken rods all along their length; instead they have rods of 1 cm at each of the four corners of the cabinet, in which grooves are made as well as in the unbroken walls (Figs. 2, 3).

2. The test solution is placed in an ordinary micro-cone [1,2], and two platinum rods fixed in it. The electrodes in this case are platinum wires ca. 0.1 mm in diameter, fused into a glass tube and insulated from each other (Fig. 4). The current is led in throught a copper wire which is pressed on to the platinum wires. Electrodes of this type are made as follows; two platinum wires (1) of the requisite length (2-2.5 cm) are connected to two copper wires (2) by pressing; the contact is made more reliable if a crystal of silver nitrate is placed at the junction between the copper and platinum and heated in a micro flame to reduce the silver. The wires thus obtained (3) are fixed in a glass capillary, only ca. 1 cm of the end of the platinum wires being left free. The whole is then mounted in a glass tube (4). A plastic cap (5), chosen so that it corresponds in diameter to the tube, is then fixed at the end of the tube where the copper wires are located, and the copper wires fixed through the cap. The platinum wires are bent as shown in Fig. 4. In this form the electrodes are ready for use.

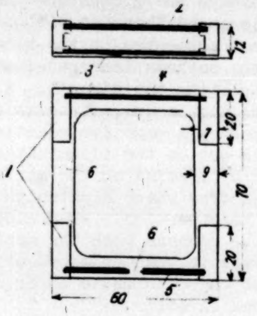

Fig. 2. Cabinet for carrying out electrolysis on the condenser rod.

1, 6 - brass walls and frame; 2, 3, 4, 5 - glass covers, bottom and walls.

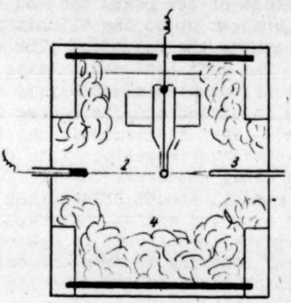

Fig. 3. Arrangement of the apparatus for carrying out electrolysis on the condenser rod.

1 - condenser rod; 2 - platinum electrodes; 3 - micro pipet; 4 - damp cotton wool.

Procedure For Electrolysis

1. Electrolysis on the condenser rod. The condenser rod and the anode fused to it are fixed to a cover glass and placed in a humidity cabinet (Fig. 3). The cabinet is fixed on the objective stage of the microscope so that its brass walls are turned toward the manipulators, while the part of the condenser rod which ends up in the surface where the electrolysis is conducted is turned toward the observer (Fig. 3). The current leads are fixed in the mercury contacts of the anode and cathode. An ordinary humidity cabinet containing the necessary micro flasks is placed on top of the cabinet containing the condenser rod set up for electrolysis.

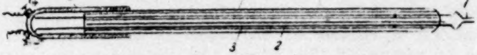

Fig. 4. Forked platinum electrodes.

1 - electrodes; 2 - copper wires; 3 - insulated capillaries; 4 - glass tube; 5 - plastic cap.

The cross-over arrangement of the cabinet thus obtained is suitable for leading the cathode up to the condenser rod, and for illuminating the latter. The illumination in this case is arranged so as to be level with the condenser rod in its cabinet, and the light falls on the surface F of the rod (Fig. 1). The piston and pipet set-up is fixed in the right hand claw of the manipulator [1]. When the apparatus has been arranged in this way we can proceed with the electrolysis. The flask (i.e. capillary tubes, etc.) which are in the upper cabinet are filled with the necessary solutions. A definite amount of the requisite solution is then sucked up in the micro pipet and removed from the cabinet; it is then lowered by means of the micro manipulator to the level of the gap in the lower cabinet.

The upper cabinet is removed and the surface of the condenser rod on which the electrolysis occurs is introduced into the field of vision, and the microscope focussed. The solution in the pipet is transferred on to the electrolysis surface. By means of the naked eye and by observation through the microscope the cathode is brought up to the illuminated surface and arranged above it without actually touching the solution. The accumulator is then connected to the electrolysis cell. The left hand manipulator is lowered and the cathode immersed in the drop on the illuminated electrolysis surface, thus completing the circuit. Electrolysis is initiated and its course followed under the microscope, (bubbles of gas are visible). That electrolysis has finished is checked by a negative reaction with the respective reagents. This reaction is carried out on the illuminated surface of the usual condenser rod [2] in another cabinet by placing on the surface of the rod a small amount of solution taken from the surface where electrolysis was carried out, and adding the respective reagent to this portion. When electrolysis is complete the circuit is opened by lifting up the cathode with the manipulator, thereby removing it from the solution. The current is then switched off. The metal which has been deposited is determined by its characteristic color, or by means of special reagents after it has been dissolved in acid.

2. Electrolysis on a micro-cone. The micro apparatus containing the requisite solutions and the micro-cone which serves as the electrolyzer are placed in the humidity cabinet. The diameter of the micro-cone should be such that, when the electrodes are inserted into it, they do not touch the walls of the micro-cone. If the electrodes are almost touching the walls, then the solution which is displaced on immersing them will flow along the walls, so that all of the solution is not electrolyzed. It is essential also that the length of the electrolyzer should not be more than 4-5 mm; in such a case only a small part of the electrodes will be located in that part of the electrolyzer not filled with solution, and which amounts to a third of its volume. The cabinet and the micro cell are fixed on the object stage of the microscope. The platinum electrodes (Fig. 4) are fixed in the left hand claw of the manipulator, while the piston set-up and pipet are fixed in the right hand claw. A volume of solution is transferred from the micro flask to the electrolyzer by means of the pipet, the volume being such that it does not occupy more than two thirds of the volume of the micro cell, in order that spilling may be avoided during electrolysis. The opened side of the humidity cabinet is turned toward the left hand manipulator and then, first by means of the naked eye and finally with the aid of the microscope, the electrodes are introduced into the electrolyzer without actually immersing them in the solution. The current is switched on and the electrodes then immersed in the solution by moving the electrolyzer on to them (Fig. 5), thereby completing the circuit. When electrolysis is finished the circuit is broken by removing the electrodes first from the electrolyzer and then from the cabinet, by means of the manipulator. Finally the current is switched off. The metals which have been electrolytically deposited in this way are detected as described above.

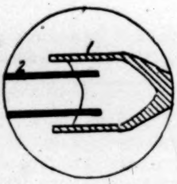

Fig. 5. Electrolysis with forked platinum electrodes (as seen under the microscope).

1 – micro-cone + electrolyte; 2 – electrodes.

b) Examples of electrolytic deposition and detection of metals

1. Deposition of copper on a platinum cathode. A solution of cupric sulfate

(1 mg/ml) was prepared in 0.2 M H_2SO_4. The current necessary is calculated from a knowledge of the surface area of the electrodes and the recommended current density. Electrolysis is carried out as described above on the illuminated surface of a condenser rod or in a micro-cone electrolyzer. The deposit of copper formed on the cathode is examined under the microscope in reflected light. If the layer of copper which separates out on the given surface is so thin that its color cannot be observed, then the electrode is immersed for some time in a flask containing nitric acid. The copper is then detected in the solution by means of either sodium diethyldithiocarbamate or rubeanic acid.

Copper can be deposited electrolytically in the same way from solutions containing other metals (e.g., iron, zinc, nickel). Results for the electrolytic separation of copper from solution are adduced in Table 1.

2. Deposition of lead dioxide on a platinum anode. A solution of lead nitrate is used (1 mg/ml of Pb). Electrolysis was carried out as described above at 2.7 V using a current of 10^{-4} A. The brown film of lead dioxide which is formed on the anode can be clearly distinguished under the microscope in reflected light. The solutions left after electrolysis gave negative reactions with dithizone. Results on the deposition of lead dioxide on a platinum anode are given in Table 1.

TABLE 1

Separation of copper and lead on platinum micro electrodes

No.	Electrolyte		Electrodes			Conditions of electrolysis			Electrolysis products	
	Composition	Metal concentration, (g/ml)	Volume, (ml)	Diameter (cm)	Surface area, in cm^2	Voltage, in V	Current, in amp.	Time, in min.	Composition	Amount, in g
1	$CuSO_4$	$1\cdot10^{-3}$	$1\cdot10^{-3}$	0.01	$\sim10^{-3}$	2.2	10^{-4}	10	Cu	$1\cdot10^{-6}$
2	$CuSO_4$ $NiSO_4$ $FeSO_4$	$1\cdot10^{-3}$ $1\cdot10^{-3}$ $3\cdot10^{-4}$	$0.5\cdot10^{-3}$ $0.5\cdot10^{-3}$ $0.5\cdot10^{-3}$	0.01	$\sim10^{-3}$	2.2	10^{-4}	10	Cu	$5\cdot10^{-7}$
3	$CuSO_4$ $NiSO_4$ $FeSO_4$ $ZnSO_4$	$1\cdot10^{-3}$ $1\cdot10^{-3}$ $3\cdot10^{-4}$ $1\cdot10^{-3}$	$0.5\cdot10^{-3}$	0.01	$\sim10^{-3}$	2.2	10^{-4}	10	Cu	$1\cdot10^{-7}$
4	$CuSO_4$	$5\cdot10^{-5}$	$1\cdot10^{-3}$	0.01	$\sim10^{-3}$	2.2	10^{-4}	10	Cu	$5\cdot10^{-8}$ 1)
5	$Pb(NO_3)_2$	$1\cdot10^{-3}$	$0.5\cdot10^{3}$	0.01	10^{-3}	2.7	10^{-4}	10-15	PbO_2	$5\cdot10^{-7}$

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1) The copper which separated out on the cathode in this case was detected after dissolving it in acid, by means of sodium diethyldithiocarbamate or rubeanic acid, since direct observation of the copper color on the cathode was impossible because the copper layer was too thin.

Electrolysis on a mercury micro cathode

Electrolysis in which a mercury cathode is employed is very widely used in analytical chemistry because it enables such metals as chromium, iron, and molybdenum, which are not deposited on platinum electrodes, to be separated. Mercury occupies a unique position as cathodic material, since it requires different apparatus and different technique. In addition, the process of electrolysis on a mercury cathode is accompanied by intense evolution of gas bubbles, and heating of the solution. These two factors give rise to a number of difficulties when working on the ultra-micro scale.

a) Apparatus

Electrolysis on a mercury cathode is carried out in a capillary open at both ends because of the intense gas formation which occurs during electrolysis and which would lead to the solution being expelled if the electrolysis were conducted in the usual type of cell.

The mercury cathode is prepared by covering a platinum fork (Fig. 4) electrolytically with mercury (in order to do this it is only necessary to join the copper leads at the place where the current is supplied to electrodes). A platinum wire fused into the same glass tube serves as the anode. In order to prepare the mercury micro cathode, a solution of mercuric nitrate (0.1 g in 0.05 ml of HNO_3 and 5 ml H_2O) is used. Electrolysis is carried out in a micro-cone until a drop of mercury is formed on the fork. Electrodes prepared in this way can be used for electrolysis on a mercury cathode (Fig. 6). The current for anode and cathode is first led from the accumulator to a switch resistance box.

b) Procedure for electrolysis on a mercury micro cathode

The micro apparatus required to hold the necessary solutions and the capillary open at both ends are placed in a humidity cabinet on a stand [1, 2]. The capillary electrolyzer should be of such a diameter that when the electrodes are introduced into it, they do not touch the walls. The cabinet is fixed on the objective stage of the microscope. The tube containing the electrodes is clamped in the left hand manipulator in such a way that the anode is above the cathode, while the piston set-up and pipet are clamped in the right hand manipulator. The micro vessels are filled with the requisite solutions and measured amounts of them transferred to the capillary, in which the solution is arranged so that it is at a distance of about a third of the length which its volume occupies from the end of the capillary turned toward the pipet. The cabinet with the opened side is then turned towards the left hand manipulator. Initially the electrodes are adjusted by means of the naked eye and finally with a microscope in the capillary electrolyte, without actually immersing them in the solution. The current is switched on and the circuit completed by moving the capillary on to the electrode until the latter just touches the farther meniscus of the solution. The course of the electrolysis is followed under the microscope. The completion of electrolysis is tested for by means of the requisite reagents. When it has finished, the electrodes are withdrawn from solution, and the current switched off.

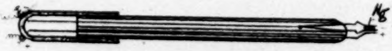

Fig. 6. Mercury micro cathode.

After deposition of the metal on the mercury cathode the mercury is removed by including the cathode in a circuit used as a micro heater [2]. The metals which remain on the fork after removal of the mercury can be dissolved by immersion in a micro-cone containing the respective solvents, and the metals subsequently detected in solution.

c) Examples of the separation of metals on a mercury micro-cathode

1. Separation of vanadium from copper and iron. Solutions of cupric sulfate, ferrous sulfate, and ammonium vanadate in 2N sulfuric acid were prepared.

The voltage normally used for macro-electrolysis on a mercury cathode cannot be recommended for the electrolysis of small volumes, since when such a voltage is used electrolysis proceeds so turbulently that within a very short time all the solution would be splashed out and evaporated. Vanadium is separated from copper and iron at a voltage of 3.3-3.8 V, with a current of $3.3\text{-}3.8 \cdot 10^{-4}$ A. Electrolysis is stopped when the electrolyte gives a negative reaction with potassium ferro- and ferricyanide. The presence of vanadium is detected by means of cupferron solution. The volumes of solutions and the amounts of material used for electrolysis are adduced in Table 2.

2. Separation of vanadium from chromium. Solutions of potassium chromate and ammonium vanadate in 2N sulfuric acid were prepared. Electrolysis was carried out as described previously at a voltage of 3.4-3.6 V and a current of $3.4\text{-}3.6 \cdot 10^{-4}$ A. Electrolysis was stopped when the solution gave a negative reaction for chromium with diphenyl carbazide. The volumes and weights of materials used are adduced in Table 2.

TABLE 2

Separation of elements by electrolysis on a mercury micro-cathode

No.	Electrolyte			Cathode surface, in cm^2	Electrolysis conditions			Deposit on cathode		Left in Solution (Qual.)	
	Composition	Metal concentration (g/ml)	Volume, in ml		Voltage, in V	Current, in A	Time, in min.	Metal	Amount, in g	Element	Amount, in g
1	$CuSO_4$	$1 \cdot 10^{-3}$	$0.5 \cdot 10^{-3}$	$2 \cdot 10^{-3}$	3.8	$3.8 \cdot 10^{-4}$	15	Cu	$5 \cdot 10^{-7}$	–	–
	$FeSO_4$	$3 \cdot 10^{-4}$	$0.5 \cdot 10^{-3}$					Fe	$1.5 \cdot 10^{-7}$	–	–
2	$CuSO_4$	$1 \cdot 10^{-3}$	$0.3 \cdot 10^{-3}$	$2 \cdot 10^{-3}$	3.8	$3.8 \cdot 10^{-4}$	15-20	Cu	$3 \cdot 10^{-7}$	–	–
	$FeSO_4$	$3 \cdot 10^{-4}$	$0.5 \cdot 10^{-3}$					Fe	$1.5 \cdot 10^{7}$	–	–
	NH_4VO_3	$2 \cdot 10^{-4}$	$0.7 \cdot 10^{-3}$					–	–	V	10^{-7}
	(H_2SO_4)										
3	NH_4VO_3	$2 \cdot 10^{-4}$	$0.5 \cdot 10^{-3}$	$2 \cdot 10^{-3}$	3.6	$3.6 \cdot 10^{-4}$	15	–	–	V	10^{-7}
	(H_2SO_4)										
	$K_2Cr_2O_7$	$2 \cdot 10^{-4}$	$0.5 \cdot 10^{-3}$					Cr	$1 \cdot 10^{-7}$	–	–

SUMMARY

1. Apparatus and methods have been developed for the electrolytic separation and detection of elements on the ultra-micro scale.

2. Procedures are described for ultra-micro electrolysis using platinum and mercury electrodes in solution with volumes of the order of 10^{-3} ml and with amounts of material of the order of 10^{-6} to 10^{-8} g.

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CRYSTALLINE LIGHT FILTERS FOR THE ULTRA-VIOLET REGION OF THE SPECTRUM [1]

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In the course of scientific research, and in seeking for the solutions of a number of practical questions, it often becomes necessary to separate fairly narrow bands in the ultraviolet region of the spectrum in the spectrum of the light source. This is usually achieved either by using monochromators, which are rather expensive and complicated, or by means of various types of light filters. The difficulties which confront investigators working in this spectral region when selecting the requisite light filters are well known, despite the fact that a large amount of work [1, 2] has been devoted to light filters suitable for the ultraviolet.

In most cases liquid light filters, which are solutions of various chemicals, are used for the isolation of individual bands in the ultraviolet. Liquid light filters, however, have rather wide transmission bands, and they considerably weaken the light isolated. Slight contamination of the solutions leads to an even greater decrease in the transmission coefficient. Many of these solutions, once exposed to the ultra-violet, deteriorate on storage, and the filters cease to transmit the necessary spectral band.

Peskov's light filter [3], in which a gaseous mixture of bromine and chlorine is used as the absorbing material, is of special interest. This filter is fairly constant, and is used for the isolation of a wide band of wave lengths in the ultra-violet from 2000-3000 A. More frequently, however, it becomes necessary to isolate a narrow band or individual lines from a line spectrum with a fairly high transmission coefficient. Gas filters are obviously unsuitable for such purposes.

In the course of the present investigation we studied the absorption spectrum of mixed crystals of the alkali halides with the objective of constructing narrow band crystalline filters for the ultra-violet.

The alkali halides find wide application in optics on account of their transparency to the ultra-violet, visible and infra red spectral regions. Good transparency, however, is a characteristic of only very pure crystals. The presence in the crystals of even insignificant amounts of impurities, sometimes not more than a thousandth of a percent, lead to supplementary absorption in the crystals. Investigation [4, 5] of the absorption spectra of crystals of the alkali halides containing various impurities has shown that in addition to the characteristic absorption bands of the crystals themselves in the ultra-violet, absorption bands which are caused by the impurities can be observed. These absorption bands are ascribed [6] to the ions of the impurity, and appear in the spectrum as the result of an electron transfer from a fundamental level of the ion to an excited level. The position of the band caused by the impurity, in the absorption spectrum of the crystal, and the form of this band, is determined by the nature of this impurity, while the absorption coefficient is determined by the amount of impurity. With increasing concentration, the impurity absorption maximum increases. One and the same impurity, when present in various alkali halide crystals, gives rise to absorption bands which are located in different parts of the ultra-violet. Thus, Tl as an impurity in KCl, KBr, and KI crystals, respectively, gives rise to maximum absorption at 2475, 2610 and 2870 A, respectively. Pb in KBr crystals gives rise to a maximum absorption in the KBr absorption spectrum at 3020 A. Pb and Tl as impurities in other crystals of the alkali halide salts also lead to the appearance of absorption bands which are characteristic of the impurity, but are located in other parts of the spectrum. In mixed crystals the position of the absorption band depends on the concentration of the components. Thus, if an impurity of a different kind is introduced into the crystals of the alkali-halide salts, it is possible to get absorption bands for the impurity at various points in the absorption spectra, according to which alkali halide salt the impurity has been added, and according to the nature of the impurity. These great possibilities of getting absorption bands at various points in the ultra-violet absorption spectrum, and also the exceptional definition of the absorption band, enable one, by using combinations of crystals with various impurities, to separate narrow transmission bands in the ultra-violet. It seemed to us, therefore, that crystals of alkali halide salts containing impurities could be used for constructing narrow band light filters for the ultra-violet.

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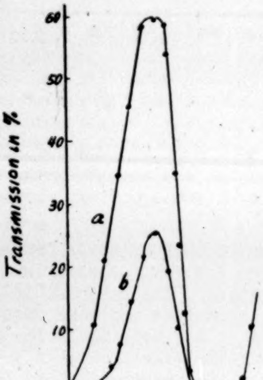
[1] Presented at the Leningrad Physico-Technical Institute, Academy of Sciences, USSR, in 1951.

When impurities are added to mixed crystals, the absorption bands which arise as a result of the presence of impurities are displaced in the spectrum (as already indicated) in accordance with the various percentages of the components of the mixed crystals; consequently, the position of the transmission band of the crystalline light filters will also be determined by the concentrations of the components of the mixed crystals. This last fact enables one, within known limits, to shift arbitrarily the transmission bands of the light filters along the spectrum, and thus makes it possible to construct crystalline light filters for the requisite wave length.



As an illustration of the possibility of constructing light filters for the ultra-violet, we adduce the absorption spectra of the mixed crystals KCl + KBr (Curve a in the diagram) containing an equal amount of the components, and Pb as an impurity. It is evident from the diagram that the mixed crystals KCl + KBr have a clear cut transmission band within the ultra-violet, with maximum transmission at 2625 A. The transmission coefficient for this wave length is more than 60%. In addition to its transparency to the ultra-violet, this crystal is transparent to light of wave length greater than 3000 A. Therefore, when the mixed crystal KCl + KBr is used as a light filter, it is necessary to use a supplementary filter, with good transmission in the 2600 A region, and which absorbs the long wave length part of the absorption spectra of the crystal (starting at 3000 A). In such a case the gas filter (considered above) which absorbs in the 3000-5000 A region can be used as a supplementary filter. The transmission of the crystal KCl + KBr and of the gas filter working together, as can be seen from the transmission curve (Curve b in the diagram), consists of only one narrow band in the ultra-violet.

Thus, an optical system consisting of the mixed crystal KCl + KBr with Pb as an impurity and the gas filter as a supplementary can be used as a light filter with a high luminosity and with a narrow transmission band. The transmission coefficient of this light filter at 2650 A amounts to 26% for a half width of the transmission band of about 170 A.

A narrower transmission band at 2600 A is given by a combination composed of a crystal of KCl containing Tl and Pb, the mixed crystal KCl + KBr containing Pb, and the gas filter. The transmission coefficient in this case at 2625 A amounts to 14% for a half width of the transmission band of only 85 A.

KI containing Tl in combination with a gas filter exhibits a maximum transmission band at 2750 A. The transmission coefficient of this light filter is 26% for a half width of the transmission band of about 200 A.

The transmission bands can be narrowed by using as a supplementary filter the mixed crystal KCl + KBr containin Tl. This crystal cuts out the short wave part of the transmission band,and,by varying the proportion of KBr, transmission bands of different widths can be obtained.

For isolating a band at 2850 A,a filter can be used which is composed of a crystal of KBr + KI (containing Tl + Pb),plus a gas filter. The transmission of the gas filter which we had at our disposal was low (ca. 25%) at 2850 A; consequently the light filter consisting of a crystal of KBr + KI and a gas filter has a transmission coefficient of only 10% at 2850 A for a half width of the transmission band of 120 A. Increasing the concentration of bromine in the gas filter increases its transmission coefficient at 2850 A,thereby leading to a possible increase in the transmission of the combination light filter.

Apart from the light filter mentioned above,we also prepared a special monochromatic light filter which isolates only the resonance line of the mercury spectrum at 2537 A. This light filter was made from a crystal of KBr containing Tl and Pb and a crystal of KCl containing Pb. The gas filter was used as the supplementary filter. This light filter had a verv narrow transmission band in the ultra-violet, the half width being only 20-30 A for a transmission coefficient of 4-5% at the maximum absorption band at 2535 A. If it is taken into account that this light filter is designed for the isolation of only the 2537 A line in the mercury spectrum and that this line makes up 80% of the intensity of all the spectrum of a mercury low pressure lamp,then the transmission of this filter will be adequate in a number of cases.

I should like to express my thanks to Prof. E.F.Gross,Corresponding Member of the Academy of Sciences of the USSR,for his constant interest in the work.

SUMMARY

In contrast to other absorbing light filters for the ultra-violet, crystalline light filters isolate a narrower spectral band with considerably less loss of light inside the transmission bands. In addition, the position of the transmission band itself can be shifted within limits along the spectrum by varying the proportions of the various components of a mixed crystal,whereby a light filter can be constructed for a chosen wave length and can be adjusted to suit actual experimental requirements.

The high transmission coefficient makes crystalline filters suitable both for investigating weak radiation as well as for getting optical images in ultra-violet light. It is evident that crystalline filters can be applied in many fields of scientific investigation; their stability to the effect of the ultra-violet,and also their constancy with time,enable crystalline light filters to be used in various types of optical apparatus.

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AN INVESTIGATION OF THE POSSIBILITY OF COLORIMETRIC ANALYSIS IN THE ULTRAVIOLET

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Contemporary colorimetry uses the absorption spectra of compounds which absorb in the 4000-7500 A region for analytical purposes. Accordingly, the colorimetric method of analysis can only be applied for the quantitative determination of intensely colored compounds and of compounds for which sufficiently selective color reactions can be chosen. At the same time, the exceptionally high sensitivity of colorimetric methods, and their fairly high selectivity, and the speed with which colorimetric determinations can be made, lead to a natural tendency to introduce colorimetric methods on an increasing scale into analytical practice.

A radical increase in the number of chemical compounds which can be analyzed by colorimetric methods can be achieved by using the ultraviolet for solving colorimetric problems. The use of absorption spectra in the near ultraviolet for the quantitative analysis of chemical compounds not only increases the number of substances which can be analyzed colorimetrically, but opens up new possibilities for colorimetric analysis without preliminary chemical treatment of the test material, by using the characteristic absorption of the test material. Application of the ultraviolet also enables more simple chemical reactions which lead to the formation of products absorbing in the ultraviolet to be used for the solution of colorimetric problems. The selectivity of the colorimetric determinations can also be considerably increased.

The number of investigations devoted to the study of the possibilities of colorimetric analysis in the ultraviolet is insignificant. The majority of them does not go beyond the construction of apparatus designed for production analysis of one compound, or at the best of a few chemical compounds [1-11]. It has been established thereby that a few substances can be determined colorimetrically by means of their characteristic absorption bands in the near ultraviolet, at concentrations of 10^{-6} to 10^{-7}%.

The main obstacle to the wide introduction to analytical chemistry of colorimetric methods based on absorption of ultraviolet radiation by compounds, is the absence of light filters for the 4000-2000 A region of the spectrum which can render the light monochromatic enough, and which possess stable spectral characteristics.

Glass of Types UFS [12], Corning [13-16], U.G. [17], isolate wide spectral bands in the ultraviolet, and do not ensure selective analysis. The small number of narrow band light filters for this part of the spectrum, which are constructed on the basis of the absorption of light by solutions [18-20], cannot be applied in colorimetry because of the variability of their spectral characteristics and their size. Heterogeneous ultraviolet light filters constructed on the principle of the selective scattering of light ensure highly monochromatic light beams, but the spectral results vary very considerably with temperature [21-23].

The problem facing colorimetry in the ultraviolet which logically arises from the huge mass of material which has been accumulated hitherto on the ultraviolet absorption spectra of chemical compounds and the small amount of study devoted to this problem naturally necessitates further work on the potentially wide use of the ultraviolet in quantitative analysis. Accordingly, the work which we have carried out along these directions can be divided into three sections: a) development of the type of apparatus designed for colorimetric work in the ultraviolet; b) a search for chemical light filters which can monochromatize the ultraviolet sufficiently well and have stable spectral characteristics; c) determination of the sensitivity, accuracy, and reproducibility of the colorimetric determination of solutions of chemical compounds by their ultraviolet absorption spectra.

Apparatus

The apparatus proposed by us previously [24] was designed for objective colorimetry in the ultraviolet. The light flow was registered by means of two vacuum antimony-cesium photoelements prepared by the LIKI fitted into the arms of a photocolorimeter. The source of ultraviolet was a small hydrogen lamp with two-way radiation, made by the "Etalon" factory. The wattage of the lamp was 80-100, and it was supplied from 127 V a.c. mains (without voltage stabilization). The colorimeter lenses were made from crystalline quartz and the windows of the photoelements of Uviol glass.

The difference in the photo currents in the photoelement circuit was amplified by Krusser's method [25], which is exceptionally simple. The cells containing the solvent and the test solution respectively were placed in front of one of the photoelements, the second photoelement functioning as a balancing attachment. Readings are made by the method of optical compensations. The scatter in the readings of the transmission of the solutions does not exceed 0.5%.

Light Filters

a) Crystalline light filters. In choosing light filters for the range 2500-3000 A, we decided to use mixed crystals of the alkali-halide salts to which Pb^{2+} and Tl^{+} had been added.

The alkali halides in a crystalline state are transparent to the ultraviolet right up to 1800-2300 A [26, 27]; when small amounts of Pb and Tl are included in the crystals, it leads, as Hilsch [27] and Koch [28] have shown, to the appearance of intensive absorption bands in the 3100-2500 A region.

A comparison of the absorption spectra of aqueous solutions of salts of the type MeH (Me = metal, H = halogen) with additions of $PbCl_2$ and TlCl [29, 30] enables one to ascribe these absorption bands to complex compounds of the type TlH_x^{-x+1} and PbH_x^{-x+2} .

The spectral characteristics of mixed crystals were first used by Stekhanov [31] for preparing solid light filters having narrow transmission bands in the 2500-2850 A region.

The low values of the half-width of the transmission bands of Stekhanov's light filters (of the order of 80-200 A) and the stability of their spectral characteristics with time are strong reasons for using these filters in colorimetric analysis.

Using Stekhanov's data, but confining ourselves to investigating mixed crystals of the composition KCl + $PbCl_2$, KBr + $PbCl_2$, and KCl + KBr + $PbCl_2$, we established that the spectra of crystals of the type KCl + KBr + $PbCl_2$ cannot be regarded as a superposition of the absorption bands of the two first crystals - Figure 1. This fact favors both the view that the absorption of light is connected with the formation in the last case of complexes of the type ($PbCl_xBr_y$), and also supports Sueda's hypothesis re the chromophoric properties of the trans groups of the form $H_1 - Me - H_2$ in the molecules of the complex compounds.

The mixed crystals of $KCl + KBr + PbCl_2$ were obtained by Kyropoylas' method [33] by growing them from a melt of the mixture of the salts on a primer fixed in the block of a water-cooled steel condenser.

By varying the composition of the mixture $KCl + KBr + PbCl_2$ we were able to supplement Stekhanov's results with the following three light filters:

1. Crystals of the composition KBr - 75%; KCl - 24.6%; $PbCl_2$-0.4%. Maximum transmission of the filter- $\lambda_{max} = 270$ mμ. For a crystal thickness of d = 3.5 mμ, transmission at the maximum was $T_{max} = 55\%$, the half width of the transmission band was $\frac{\Delta\lambda}{2} = 200$ A.

2. Crystals of the following composition; KBr - 20%; KCl - 79%; $PbCl_2$ - 1%. For $\underline{d}$ = 4 mm $\lambda_{max} = 2600$ A; T_{max} - 50%; $\frac{\Delta\lambda}{2} = 150$ A.

3. Crystals: 8% KBr + 90.8%; KCl + 1.2% $PbCl_2$. $\lambda_{max} = 2570$ A, for $\underline{d}$ = 2.5 mm; $T_{max} = 70\%$; $\frac{\Delta\lambda}{2} = 230$ A.

The crystals enumerated above, just like those prepared by Stekhanov, pass light of wave length 3200 A, which was then separated by Stekhanov by the use of Peskev's supplementary gas filters [3, 4], absorbing in the region 3200 to 5000 A.

The gas filter is not suitable for colorimetric analysis, both because of its size and also because of its transparency to light of $\lambda > 5000$ A. Using Ottmer's data as a basis, we tried to replace the gas filter by a disc cut from a crystal of NaF which had been coated by heating in sodium or potassium vapor. However, as the amount of crystalline NaF at our disposal was limited, we, in parallel with Stekhanov, only carried out preliminary work on investigating a similar light filter, the spectral characteristic of which is given in Fig. 2. When working with a crystalline light filter of the composition given above we had to use, temporarily, a liquid light filter of the composition; 1.1 mol/liter Cl_2 + 0.14 mol/liter Br_2 in CCl_4. The thickness of the solution layer was 0.5 mm. One of the windows of the cell was made from UFS-1 glass, of d = 2mm. The spectral characteristic of this light filter is shown in Fig. 2, in comparison with the transmission curve for UFS-1 glass.

Crystals obtained in combination with such a filter are not transparent in the 3000 - 6700 A region; the maxima of their transmission curves lie at 2570, 2600 and 2700 A. The transmission at the maximum has values ranging from 100 to 15%. The half width of the transmission band is 80 to 160 A. The transmission curves are shown in Fig. 4.

b) Borate Glasses. In order to make light filters for the 3000 to 4000 region we made some experiments on the absorption spectra of borate glasses containing traces of heavy metals. These have not been studied in detail from an optical point of view. Some of the results obtained are given in Fig. 3.

The following light filters were prepared on the basis of similar glasses:

1) Glass of the composition: Na_2O — 30.7%; B_2O_3 — 69.1%; K_2CrO_4 — 0.2%. $\lambda_{max} = 310$ mμ; d = 1 mm; $T_{max} = 15\%$, $\frac{\Delta\lambda}{2} = 18$ mμ.

2) Glass of the composition: Na_2O — 30.75%; B_2O_3 — 69.14%; K_2CrO_4 — 0.1%; MnO — 0.001%. $\lambda_{max} = 315$ mμ; d = 1 mm; $T_{max} = 18\%$; $\frac{\Delta\lambda}{2} = 20$ mμ.

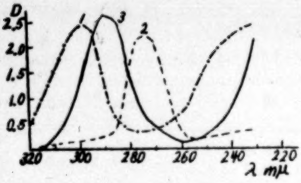

Fig. 1. Absorption curves for mixed crystals. 10 KBr + 0.6% $PbCl_2$; 2) KCl + 0.6% $PbCl_2$; 3) 50% KCl + 50% KBr + 0.6% $PbCl_2$.

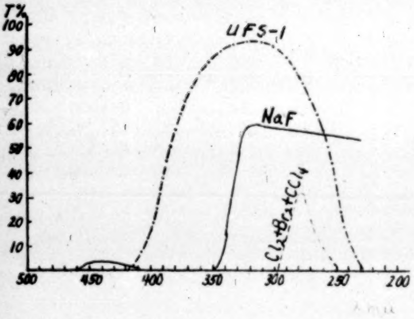

Fig. 2 Transmission curves

Glass UFS-1 (d = 2mm); crystal of NaF coated in Na vapor; liquid filter 1.1 mol/l Cl_2 + 0.14 mol/l Br_2 in CCl_4; (d = 0.5 mm)

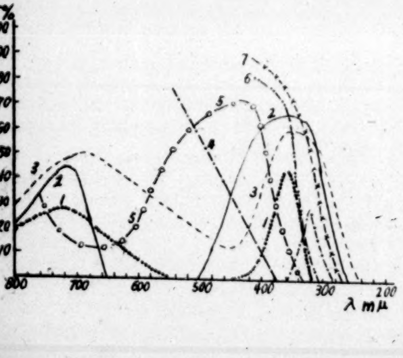

Fig. 3 Transmission curves for borate glasses

1 - Na_2O - 30.70%; B_2O_3 - 68.94%; MnO - 0.36% 2 - Na_2O - 30.66%; B_2O_3 - 68.87%; CoO - 0.47%; 3 - Na_2O - 30.7%; B_2O_3 - 68.9%; NiO - 0.4%; 4 - Na_2O - 30.78%; B_2O_3 - 69.17% K_2CrO_4 - 0.5%; 5 - Na_2O - 30.66%; B_2O_3 - 68.88%; CuO - 0.46%; 6 - Na_2O - 30.76%; B_2O_3; - 69.17%; FeO3 - 0.07%; 7 - Na_2O - 30.50%; B_2O_3 - 68.54%; PbO - 0.96%

3. Glass of the composition: Na_2O 30.72%; B_2O_3 69.01%; K_2CrO_4 0.1%; MnO 0.17%. λ_{max} = 320 mμ; T_{max} = 14%; $\frac{\Delta\lambda}{2}$ = 20 mμ.

4. Glass of the composition: Na_2O 30.67%; B_2O_3 68.92%; K_2CrO_4 0.07%; MnO 0.34%. λ_{max} = 330 mμ; d = 1 mm; T_{max} = 18%; $\frac{\Delta\lambda}{2}$ = 28 mμ.

5. Glass of the composition: Na_2O 29.98%; B_2O_3 68.02%; MnO 2%. Maximum transmission is located at λ = 355 mμ; d = 1 mm; T_{max} = 18-20%; $\frac{\Delta\lambda}{2}$ = 30 mμ.

The transmission curves for these light filters are given in Fig. 4.

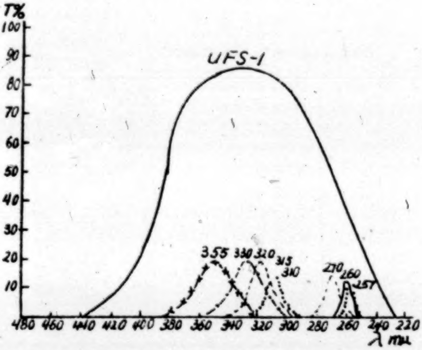

Fig. 4. Transmission curves for the light filters.

Colorimetric Determination in the Ultraviolet

The experiments which we carried out along this direction were not aimed at developing a method for the determination of any particular chemical compound, though the results given below could be used for a number of chemical analyses without essentially changing the colorimetric methods which we adopted. Any work on colorimetric analysis in the ultraviolet should evaluate the suitability of the apparatus and the light filters for carrying out analytical work in the spectral region 4000-2000 A, and also aim at determining the sensitivity and accuracy of such analysis. For this purpose, we chose some organic compounds suitable for colorimetric analysis, with intensive absorption bands in the ultraviolet, and also compounds having no absorption bands in the 2000-4000 A region. In the first case, which is the most suitable for colorimetric analysis, the determination is carried out directly with the help of the characteristic absorption of the substance, while in the second case a simple chemical reaction, in which the test compound is converted into a product which absorbs intensely in the ultraviolet, preceeds the colorimetric determination.

Benzene. The most sensitive method for the determination of benzene, which is based on the nitration to dinitrobenzene followed by colorimetric estimation of the latter in acetone solution with addition of alkali, enables quantitative analysis to be carried out right down to concentrations of benzene in the sample of the order of 10^{-4}% [36,37]. The experimental error amounts to 50%, and the analysis takes considerable time. We carried out colorimetric determinations of benzene in ethyl alcohol without any preliminary chemical treatment in a 5 cm cell with a light filter of λ_{max} = 260 mμ. Some of the analytical results, which are adduced in Table 1, demonstrate that even when working on the "edge" of the absorption band for benzene, i.e., at a known low sensitivity for colorimetric determination, it is still possible to determine the content of benzene in solution, down to concentrations of the order of 10^{-3}%, with reasonable accuracy.

Naphthalene. Methods for the quantitative determination of naphthalene which are based on its condensation with picric acid [38-39], on its nitration to nitronaphthalene or to trinitronaphthalene [40], and which are used for the analysis of coke-oven gas, for the analysis of air in factories, and in food products, enable it to be determined in amounts of 10^{-1} to 10^{-3}% in the test material. A long time is necessary for these analyses.

We made colorimetric determination of naphthalene solutions using a light filter with λ_{max} = 315 mμ, i.e., on the long wave side of the absorption band. The sensitivity of the analysis decreases with other filters, but benzene and its homologs do not interfere.

Results of the analysis carried out in a 5 cm cell are given in Table 2. The lower limit of the concentration, determined with a relative error of 6%, is ca. 10^{-4}%.

Anthracene. The most sensitive spectrophotometric method for the determination of anthracene in petroleum [41] allows it to be determined in concentrations of the order of 10^{-3}%.

TABLE 1

Benzene in Ethyl Alcohol

Benzene taken, in %	Benzene found, in %	$\Delta c/c$, %
0.050	0.047	6
0.040	0.041	2.5
0.030	0.032	7
0.021	0.022	5
0.015	0.016	6
0.010	0.010	0
0.0049	0.0047	6
0.0025	0.0023	8

TABLE 2

Naphthalene in Ether

Naphthalene taken, in %	Naphthalene found, in %	$\Delta c/c$, %
0.00075	0.00075	0
0.00068	0.00065	5
0.00060	0.00062	3
0.00050	0.00048	4
0.00045	0.00047	3
0.00040	0.00038	5
0.00023	0.00024	4
0.00017	0.00018	6

Results are given in Table 3 for the colorimetric determination of anthracene solutions using its characteristic absorption in the ultraviolet. The light filter used had λ_{max} = 355 mμ.

Nitrobenzene. By converting nitrobenzene into dinitrobenzene and carrying out a colorimetric analysis on the colored solution of the dinitrobenzene in acetone in the presence of alkali, it is possible to determine it quantitatively, at concentrations down to 10^{-4}%, with an error of up to 50% [36]. The method is not specific; benzene, toluene and xylene interfere.

In our experiments, the results of which are given in Table 3, we used the characteristic absorption of nitrobenzene in the ultraviolet. A light filter with λ_{max} = 315 mμ, i.e., outside the region of absorption by hydrocarbons of the benzene series, was used for the colorimetric determination. A determination takes 5-10 minutes, and the sensitivity is increased considerably.

Aniline. Small amounts of aniline are usually determined colorimetrically by means of the blue solutions which are formed by its oxidation with chloramine in the presence of phenol [36]. The lower limit of the concentration which can be determined quantitatively is of the order of 10^{-5}%. The error of the method amounts to 50% and ammonia and toluidine interfere.

It is possible to determine aniline colorimetrically with the same sensitivity, but with a smaller error, by its characteristic absorption in the ultraviolet.

Results of analysis which we carried out using a light filter with λ_{max} = 275 mμ for a cell length of 5 cm are given in Table 5.

Pyridine, quinoline. Colorimetric determinations of aqueous solutions of pyridine (Table 6), and of solutions of quinoline in ether (Table 7), using filters with λ_{max} = 260 mμ and λ_{max} = 315 mμ, demonstrated the possibility of determining both compounds quantitatively by means of their absorption spectra in the ultraviolet at concentrations of the order of 10^{-4}%. The experimental error does not exceed 10-12%.

TABLE 3

Anthracene in Ether

Anthracene taken, in %	Anthracene found, in %	$\Delta c/c$, %
0.00017	0.00017	0
0.000113	0.000112	1
0.000050	0.000047	6
0.000034	0.000032	6
0.000020	0.000021	5
0.000015	0.000014	6
0.0000085	0.0000090	6
0.0000056	0.0000050	12

TABLE 4

Nitrobenzene in Ether

Nitrobenzene taken, in %	Nitrobenzene found, in %	$\Delta c/c$, %
0.00050	0.00048	4
0.00027	0.00026	4
0.00020	0.00019	5
0.00010	0.00011	10
0.00008	0.00008	0
0.00007	0.00007	0
0.000045	0.000040	11

TABLE 5

Aniline in Water

Aniline taken, in %	Aniline found, in %	$\Delta c/c$, %
0.00125	0.00125	0
0.00055	0.00056	2
0.00040	0.00042	5
0.00023	0.00023	0
0.00015	0.00016	6
0.000080	0.000085	6
0.000059	0.000060	1.5
0.000050	0.000040	20

TABLE 6

Pyridine in Water

Pyridine taken, in %	Pyridine found, in %	$\Delta c/c$, %
0.0150	0.0145	3
0.0080	0.0084	5
0.0050	0.0049	2
0.0030	0.0030	0
0.00155	0.00150	3
0.00100	0.00102	2
0.00080	0.00075	7
0.00051	0.00045	12
0.00030	0.00032	7

TABLE 7

Quinoline in Ether

Quinoline taken, in %	Quinoline found, in %	$\Delta c/c$, %
0.00575	0.00580	1
0.00290	0.00280	3
0.00200	0.00200	0
0.00115	0.00110	5
0.00060	0.00063	5
0.00046	0.00043	7
0.00015	0.00018	20

TABLE 8

Carbon Disulfide in CH_4

Carbon disulfide taken, in %	Carbon disulfide found, in %	$\Delta c/c$, %
0.0183	0.0185	1
0.0075	0.0073	3
0.0044	0.0043	2.5
0.0026	0.0025	4
0.00101	0.00105	4
0.00069	0.00072	4
0.00050	0.00055	10
0.00040	0.00045	11

Carbon Disulfide. Small amounts of carbon disulfide are usually determined colorimetrically after conversion into colored copper dithiocarbamate. The sensitivity of such determinations amounts to 10^{-3}-10^{-4}% for a relative experimental error amounting to 50% [36].

We used its absorption of light of wave length 315 mμ for its determination. The results adduced in Table 8 indicate the high accuracy of this method. H_2S, which does not absorb in this spectral region, does not interfere.

Acetone, methylethylketone, and methylpropylketone. The lower limit of acetone concentration which can be determined by Messinger's method [42] is of the order of 10^{-3}%. The method based on the action of hydroxylamine hydrochloride on a sample containing the acetone, with subsequent titration of the HCl generated, has a similar sensitivity.

The absorption spectra of the aliphatic ketones include absorption bands at 270 mμ. The numerical values of the absorption coefficients, however, are insignificant, and enable ketones to be determined at concentrations of 10^{-2}% and higher in the test sample.

Messinger's reaction is characterized for aliphatic ketones of the type $CH_3 — CO — R$, whereby iodoform is obtained which has an exceptionally intense absorption band at 350 mμ. We used this fact as a basis for the colorimetric determination of small amounts of acetone, methylethylketone, and methylpropylketone.

20 cm^3 of a solution of the composition 200 g KI +100 g I_2 + 400 cm^3 water are measured into a 100 cm^3 separating funnel, and 6.6 cm^3 of 20% NaOH and 20 cm^3 of the solution to be tested for its ketone content added.

The mixture is shaken vigorously for 5 minutes, after which excess is destroyed by addition of 0.1 cm^3 of 5% $Na_2S_2O_3$, and the iodoform extracted with 20 cm^3 chloroform.

After 10 minutes standing, the chloroform is poured into the cell and the iodoform determined colorimetrically, using a light filter with λ_{max} = 355 mμ and a cell length of 5 cm.

The analytical results are given in Tables 9-11.

Aliphatic alcohols. Data on the sensitivities of various analytical determinations of small amounts of aliphatic alcohols are contradictory [36-44]. The lowest concentration which can be determined fairly accurately is ca. 10^{-3}%. Vorokhobin's method [45], when carefully followed, enabled the author to determine the concentration of ethanol in biological media down to concentrations of $5 \cdot 10^{-4}$% with an experimental error of the order of 10%.

Nizovkins's colorimetric method is complicated and leads to considerable loss of material [46].

For carrying out colorimetric determinations of solutions of methyl, ethyl, isopropyl, n-butyl and n-octylalcohols, we used the absorption spectra of the alkyl nitrites obtained by the action of nitrous acid on the respective solutions. These absorption bands occur at 370 mμ and 355 mμ. The procedure adopted was as follows; 20 cm^3 of the test solution, 1 cm^3 of 5N HCl, and 20 cm^3 of aviation gasoline [washed several times with H_2SO_4 (d = 1.84), NaOH solution and water] were placed in a 100-ml separating funnel, to which was quickly added 2 cm^3 of $NaNO_2$ solution, and the funnel shaken vigorously for 5 minutes. The gasoline layer was poured into a second separating funnel and shaken up with 20 cm^3 of 0.1 N NaOH for 5 minutes. The gasoline containing the alkyl nitrite was then poured into a 2 cm length cell and determined colorimetrically, using a light filter with λ_{max} = 355 mμ.

The results of these analyses are given in Tables 12-16.

SUMMARY

1. Using borate glass, ultraviolet light filters were made with maximum transmissions at 310, 315, 320, 330, and 355 mμ. In addition to Stekhanov's light

TABLE 9

Acetone in Water

Acetone taken, in %	Acetone found in %	Δ c/c, %
0.00094	0.00093	1
0.00042	0.00041	2.5
0.00021	0.00020	5
0.00017	0.00018	6
0.000130	0.000125	4
0.000068	0.000070	3
0.000053	0.000050	6
0.000033	0.000035	8

TABLE 10

Methylethylketone in Water

Methylethylketone taken, in %	Methylethylketone found, in %	Δ c/c, %
0.00067	0.00066	1.5
0.00040	0.00039	2.5
0.00034	0.00035	3
0.00025	0.00025	0
0.00018	0.00020	10
0.00010	0.00011	10
0.000065	0.000060	11
0.000032	0.000028	13

TABLE 11

Methylpropylketone in Water

Methylpropylketone taken, in %	Methylpropyl- found, in %	Δ c/c, %
0.00031	0.00030	3
0.00022	0.00021	5
0.00015	0.00015	0
0.000110	0.000105	5
0.000095	0.000090	6
0.000075	0.000075	0
0.000040	0.000035	12
0.000018	0.000020	11

TABLE 12

Methyl alcohol in Water

Methyl alcohol taken, in %	Methyl alcohol found, in %	Δc/c, %
0.0200	0.0202	1
0.0116	0.0110	6
0.0085	0.0086	1.5
0.0058	0.0058	0
0.0046	0.0043	6
0.0030	0.0032	7
0.0022	0.0023	5
0.00085	0.00080	6

TABLE 13

Ethanol in Water

Ethanol taken, in %	Ethanol found, in %	Δc/c, %
0.0360	0.0354	2
0.0225	0.0224	0.5
0.0090	0.0096	7
0.0068	0.0064	6
0.0051	0.0051	0
0.0036	0.0040	10
0.0018	0.0020	10
0.0008	0.0007	12

TABLE 14

Isopropyl Alcohol

Isopropyl alcohol taken, in %	Isopropyl alcohol found, in %	Δ c/c, %
0.0375	0.0370	1.5
0.0100	0.0096	4
0.0066	0.0062	7
0.0042	0.0039	5
0.0020	0.0020	0
0.00125	0.00130	4
0.00080	0.00087	9
0.00040	0.00046	15

filters, crystal filters were also constructed which could isolate narrow parts of the spectrum at 257, 260 and 270 mμ.

2. Using a number of organic compounds as examples, the possibility has been demonstrated of carrying out highly sensitive colorimetric determinations by means of the characteristic absorption of these compounds in the ultraviolet. In addition, it has been shown how it is possible to use simple chemical reactions

which give rise to the formation of products which absorb the ultraviolet intensely, for ultraviolet colorimetry.

TABLE 15

n-Butyl Alcohol

Alcohol taken, in %	Alcohol found, in %	$\Delta c/c$, %
0.0300	0.0293	2.5
0.0130	0.0135	4
0.0090	0.0092	2
0.0056	0.0054	4
0.0033	0.0030	10
0.0022	0.0024	9
0.0011	0.0013	18
0.00050	0.00058	16

TABLE 16

n-Octyl Alcohol

Alcohol taken, in %	Alcohol found, in %	$\Delta c/c$, %
0.0317	0.0320	1
0.0096	0.0090	7
0.0079	0.0082	4
0.0053	0.0048	9
0.0032	0.0032	0
0.0016	0.0015	6

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1) See Consultants Bureau English Translation, page 215.

APPLICATION OF THE ULTRAVIOLET IN ANALYTICAL CHEMISTRY

3. A PHOTOMETER FOR ULTRAVIOLET COLORIMETRY

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The colorimeters and photometers which are in use at the present are adapted for working in the visible part of the spectrum, 750-400 mμ. For this purpose the following conditions must be satisfied:

1) the compound which is to be determined colorimetrically must be intensely colored;

2) the color of the compound must remain constant with time;

3) the solution which is to be analyzed colorimetrically should not contain colored compounds which can give rise to colors with the reagents.

These conditions are not always satisfied, so that the number of compounds which can be determined colorimetrically is restricted. The colorimetric determination of compounds having a yellow color or only very weakly colored is very difficult, while the colorimetric determination of colorless compounds is impossible.

By extending the spectral region used for colorimetry on the short wave length side, it becomes possible to increase the number of compounds which can be determined colorimetrically considerably.

By observations in the ultraviolet, it is often possible to use the absorption of rays by a complex of simple composition, or even of a simple compound which is colorless or only slightly colored in the visible part of the spectrum.

Some substances which interfere during colorimetric determinations by the normal method do not interfere in the ultraviolet, since their absorption spectra at certain wave lengths are characterized by a minimum absorption of the ultraviolet. Knowing the spectral characteristic of light absorption by solutions of various compounds, we can simplify the analysis considerably and reduce to a minimum the necessity of a preliminary separation of interfering elements.

If a cell containing a substance which absorbs the ultraviolet is placed in the path of ultraviolet rays, then on examining the cell through a fluorescent screen we see a weakening of the photoluminescence of the screen [1, 2]. If the test substance does not absorb the ultraviolet, then the photoluminescence of the screen remains unchanged. Thus, by having two fluroescent screens of equal intensity, we can estimate the extent of the absorption of the ultraviolet by the substance by placing the substance between the source of light and one of the screens, and examining the two screens simultaneously.

In the ultraviolet, in contrast to colorimetry in the visible spectrum, we are comparing not a characteristic color of the test solution, but the intensity of the photoluminescence of a screen, which is dependent on the extent of the absorption of light by the test substance in the given spectral region. Thus, we are rid of the necessity of satisfying certain conditions which must be observed in the visible spectrum.

On this principle of measuring the intensity of the photoluminescence according to the extent of the absorption of the ultraviolet by the test solution, a visual photometer has been constructed for the ultraviolet part of the spectrum.

The photometer proposed consists of the following basic parts; an ultraviolet source, an object stage with a quartz plane parallel cell, interchangeable objectives with fluorescent screens, and stands for carrying the photometric set-up.

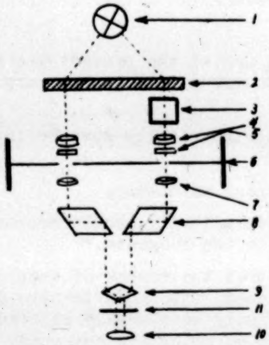

Fig.1. Schematic diagram of a photometer for colorimetry in the ultraviolet.

1) Light source; 2) and 11) light filters; 3) cell; 4) and 7) objectives; 5) florescent screens; 6) diaphragms; 8) and 9) prisms; 10) eyepiece.

The path which the rays follow and the experimental technique used for operating the ultraviolet photometer are clear from a consideration of the principal features of the set-up,as illustrated in Fig. 1.

The ultraviolet rays emitted by the light source 1, pass through a light filter 2, which removes the visible part of the spectrum from the radiation from the light source, leaving the part at 365-380 mμ. Subsequently, part of the ultraviolet rays falls directly on the objective of the photometric set-up 4, while the other part passes first through the cell containing a solution of the test material 3, and then on the objective 4. A layer of fluorescent material is superimposed on the back side of the objectives, which fluoresces only when ultraviolett light falls on it.

During the passage of the ultraviolet rays through the cell containing the test material, some of these are absorbed if the test material absorbs ultra violet-light of the given wave length, so that the photoluminescence of the objective will accordingly weaken more than the photoluminescence of the objective on which the ultra-violet rays fall directly.

In order to compare the intensities of the photoluminescence of the respective objectives, the apparatus is fitted with diaphragms 6, mounted on drums, and graduated in terms of the optical density of the solutions of the test material and the percentage transmission. Having passed through the diaphragms, the rays fall on the internal objectives 7, which serve as a control for ensuring that the rays are parallel, and then through the rhombic prisms 8, which bring the rays closer together. From the rhombic prisms the two sets of rays which have been brought close together fall on an acute-angled prism 9, which converges the rays closely so that the right-hand beam is visible in the eyepiece on the left-hand side of the illuminated field, while the left-hand beam is visible on the right-hand side of the eyepiece. From the acute-angled prism the rays fall on the eyepiece 10. Thus, in the eyepiece we can see two illuminated halves, which are not illuminated directly in the normal fashion from the source of light, but as a result of the photoluminescence of the screens.

If the test sample does not absorb the ultraviolet of a given wave length, then both halves of the field will be equally illuminated. If it does absorb, then one half will be darker than the other. By rotating the drums attached to the stops, it is possible to equalize the intensities of the photoluminescences. The reading of the drum immediately gives the optical density and the amount of light transmitted, since the change in the amount of absorption of the ultraviolet rays of a given wave length by the substance is proportional to a change in the intensity of the photoluminescence.

Various regions of the ultraviolet spectrum can be chosen according to the absorption spectra of the test material. In order to do this the ultraviolet source can be changed. Thus, for the 365-380 mμ region the PRK-4 lamp or SVDSh-250 with UFS-3 light filters can be used; while for the 313 mμ region the PRK-4 with liquid light filters (a solution of potassium chromate in water) is suitable; and for the 254 mμ region, a bactericidal lamp fitted with a UFS-1 filter can be used.

When the region of the ultraviolet to be used is changed, the fluorescent screens must also be changed, since they are excited by lines of definite wave length in the ultraviolet.

In the set-up which we have adopted, we used screens excited by rays of wave length of ca. 365 mμ, consisting of $ZnS \cdot Cu$, $ZnS \cdot Sb$, Mn; and screens of uranium glass and $Ca_3(PO_4)_2$, $F \cdot Bi$, Mn, for the 313 mμ region. Uranium glass can also be used for the ultraviolet region of 254 mμ.

When working in the 313 mμ region or in the shorter wave length regions of the ultraviolet, the fluorescent material is applied to the objective on the outer and not the inner side, since the glass of the objective completely absorbs ultraviolet rays of these wave lengths and no photoluminescence would be observed. When working in the 365 mμ region of the ultraviolet, the fluorescent material must be applied on the inner side of the objective in order that the monochromatic character of the excited photoluminescence be preserved (so that it should only be that from the 365 mμ region), since the fluorescent materials are excited by other regions to only a very insignificant extent.

The color of the photoluminescence will vary with the fluorescent material employed. It is best to choose fluorescent material which fluoresces with a white or a pale yellow color (the eye becomes less fatigued). A green light filter 11 may be introduced between the acute-angled prism 9 and the eyepiece 10, in order to increase the sensitivity.

The sensitivity of determinations carried out on our photometer exceeds that of visual measurements in the visible spectrum using the systems used at present in colorimeters and photometers, and is frequently equivalent to photoelectric methods. The mean sensitivity is 0.2-0.3 μg/ml.

As an example of the practical application of the photometer, we adduce below a method which we developed for the colorimetric determination of traces of iron in cobalt, using the photometer described above in the ultraviolet region.

The colorimetric determination of traces of iron in the presence of large amounts of cobalt is difficult in the visible spectrum because the measurements of the color intensity of the iron complexes must be carried out in the 430-450 mμ region, while in this region absorption bands of cobalt salts are also located (Fig. 2).

When iron is determined as the thiocyanate complex, the interfering action is even more strongly pronounced, because of the formation of a cobalt thiocyanate complex.

From the absorption curves it is clear that cobalt does not interfere with the determination of iron if light of wave length $\lambda = 365$ mμ is used, since these rays are not absorbed by cobalt salts, while at the same time the absorption coefficient of the ferric thiocyanate complex remains high.

In order to determine iron in the presence of large quantities of cobalt, therefore, in this part of the spectrum we used the ultraviolet photometer described above.

The experimental procedure was as follows;

The test solution containing iron was placed in a 25 ml standard flask and acidified with 0.5 ml of HNO_3 (1:1); 2.5 ml of a 10% solution of potassium thiocyanate was then added, and the volume made up to the mark.

This solution was then transferred to the quartz plane parallel cell (25 ml capacity) in the ultraviolet photometer, and its optical density measured. Having measured the optical densities of a series of a series of solutions with varying iron concentrations, we constructed a calibration curve relating optical density (D) to iron concentration (Fig. 3).

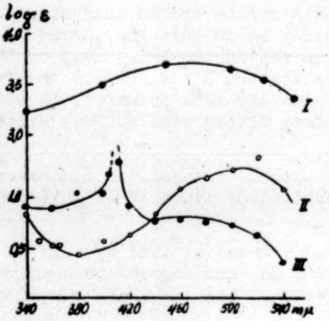

Fig.2. Absorption curves for solutions of ferric, cobalt and nickel thiocyanates. I) $Fe^{3+} + CNS^-$; II) $Co^{2+} + CNS^-$; III) $Ni^{2+} + CNS^-$.

Measurements carried out by means of the calibration curve showed that by means of this method it is possible to determine iron in amounts of from 0.005 to 0.2 mg in 25 ml with a relative error of 1-2% (Table 1).

Results for the determination of iron in solutions of its pure salts and in the presence of nickel and cobalt are given in Table 2.

Cobalt does not interfere with the iron determination in amounts of up to 75μg per 25 ml solution. Nickel should not be present in amounts of more than 7.0μg per 25 ml.

The separation of iron from a solution containing cobalt and some nickel can be effected by coprecipitation of ferric hydroxide with the basic salts of these elements. For this purpose ammonia[1] is added to the weak acid solution of the elements till a small amount of precipitate is formed, which contains the basic salts of nickel and cobalt. The precipitate contains all the iron originally in solution (a colorimetric test on the filtrate for iron gave negative results).

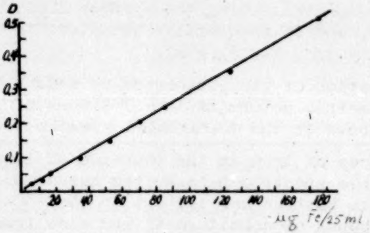

Fig.3. Calibration curve.

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[1] The ammonia solution itself should not contain traces of iron. If it does, then a blank test must be made in which the iron is coprecipitated from the amount of ammonia to be used, by means of basic cobalt salts.

TABLE 1

Fe taken, in μg	Fe found, in μg	Relative error, in %
17.6	17.2	2.0
52.8	52.5	0.6
88.0	86.5	1.7

The filtrate is filtered off, washed with water, and washed from the filter paper into a beaker. The precipitate is then dissolved by an addition of 0.5 ml of HNO_3 (1:1). The solution obtained is transferred to a 25 ml standard flask, and 2.5 ml of 10% potassium thiocyanate added; then it is made up to the mark with water. After mixing, the solution is transferred to the photometer cell, and the optical density determined. From the calibration curve the concentration of iron which corresponds to the optical density determined for the solution can then be found.

TABLE 2

Fe taken, in μg	Co taken, in μg	Ni taken, in g	Fe found, in g	Relative error, in %
17.6	49.73	-	17.8	1.1
17.6	74.60	-	18.0	2.2
35.2	-	6.57	35.2	-
35.2	-	7.39	38.0	8.0
35.2	49.73	6.57	35.0	0.6

In conclusion we should like to express our deepest gratitude to Prof. Yu. V. Morachevsky for his advice in carrying out the work.

SUMMARY

1. The principles of colorimetry in the ultraviolet are described.

2. The construction of a photometer for ultraviolet colorimetry is described.

3. A method is described for the determination of traces of iron in cobalt bymeans of ultraviolet colorimetry.

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THE POLAROGRAPHY OF FUSED SALTS

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The nature of fused salts has attracted the attention of physical chemists and analysts for a long time. Practically all the methods of physico-chemical analysis have been widely applied for the study of fused salts. These include measurements of the electro-conductivity, viscosity, and electromotive force, etc. Nevertheless, none of these methods enables the presence of any particular ion to be established in the fused salts, or enables ionic processes occuring in the fused salts to be investigated. The attempts to use the polarographic method, which has found wide application for the study of solutions, for investigating fused salts are of particular interest. The American research workers Steinberg and Nachtrieb [1] mechanically carried over the practice of polarography with the mercury dropping electrode to the study of fused salts. Their work showed the limitations of polarography with the mercury dropping electrode. Only fused salts with temperatures not exceeding 180-200° can be investigated by this method. Considerable successes have been attained in the polarography of fused salts by the use of solid electrodes. In a number of researches which we carried out during 1947-1952 [2,3,4], we demonstrated the possibility of carrying out polarographic determinations on a number of cations, using fused salts as the supporting electrolytes, over the temperature range 200-1000°. Other authors [5,6] have confirmed our findings.

The fundamental question in the polarography of fused salts is that of the supporting electrolyte to be used. If one is to draw a complete analogy between the polarography of solutions and fused salts, one should select such a fused salt that it would by itself be a non-conductor for electricity, but by readily dissolving salts of the alkali metals it would become an electrical conductor. Of the inorganic salts, fused $ZnCl_2$, AlI_3 and certain others possess such properties. Thus, Izbekov and Nizhnik [6] obtained the following results for the electrical-conductivity in the system AlI_3 - KI:

% KI	0	1.58	3.68	7.78
χ in mhos	$2.34\cdot10^{-6}$	$5.52\cdot10^{-4}$	$2.68\cdot10^{-3}$	$8.42\cdot10^{-3}$

As can be seen, addition of KI leads to a sharp increase in the electrical conductivity of the fused salt. The use of $ZnCl_2$ as a supporting electrolyte for polarography has not been a success. Obviously as the result of the very slow removal of moisture from this salt when fused, its electrical conductivity is too high immediately after fusion without any KCl being added. In addition, because of the high viscosity of fused $ZnCl_2$, it is very difficult to handle. Further work should clarify the applicability of this salt as a suitable supporting electrolyte for polarographic work. Basically for the polarography of fused salts it is the easily-fusible alkali-metal salts which have been used, the cations of which are reduced at sufficiently negative potentials on a platinum electrode. The high electrical conductivity of these salts necessitates taking special precautions for suppressing condenser currents. Using these salts as supporting electrolytes, it is possible to carry out polarographic determinations of ions reduced at potentials down to −10 V. Below this potential a general increase in the voltage-current curve of the supporting electrolyte occurs, and it becomes impossible to determine the wave height.

Ions in fused salts can be determined by means of various types of electrodes. Micro-electrodes, rotating electrodes, and the dipping electrode which we have suggested give equally good results. Micro-electrodes give small diffusion currents, so that at low concentrations determination becomes difficult. The rotating electrode gives considerably larger diffusion currents, but from the point of view of construction its application is very difficult. When working at high temperatures it is difficult to avoid vibrations of the electrode, which distort the polarographic process. Considerable difficulties also arise when changing the fused salts. In our opinion, the dipping electrode is the most suitable for studying the polarography of fused salts. Fundamental work has been carried out by means of this electrode, although both the micro-electrode and the rotating electrode have also been used for some determinations.

All these types of electrodes can be used for polarographic analysis by utilizing the following types of diffusion currents:

1) "throw" current, which is formed right at the very moment when the potential is applied;

2) "stable" current, established within 3-5 minutes after applying the potential;

3) polarographic current, formed for a definite rate of application of the potential.

The "throw" current corresponds to the smallest thickness of the diffusion layer, and has the greatest value. The "stable" current corresponds to the greatest thickness of the diffusion layer and has the least value. The polarographic current has an average value and its magnitude depends on the rate at which the potential is applied. For purely analytical purposes, the polarographic current is the most suitable. The "throw" and "stable" currents are of theoretical interest. In the majority of the cases cited below it was the polarographic current that was used.

Fused nitrates were first used as the supporting electrolytes for the polarographic determinations. The advantage of these as supporting electrolytes is the comparatively low fusion temperature; the eutectic ternary melt KNO_3-$NaNO_3$-$LiNO_3$ has a fusion temperature of about 140°. Its disadvantage is the ease with which the nitrates decompose at high temperatures. According to their behavior during polarographic determinations, all cations can be divided into three groups:

1) ions, the nitrates of which are stable at the temperature at which the analysis was carried out: Ag^+, Cd^{2+}, Pb^{2+};

2) ions, the nitrates of which are of low stability at the polarographic temperature: Cu^{2+}, Ni^{2+}, Co^{2+} and Hg^{2+};

3) ions, the nitrates of which are unstable: Fe^{3+}, Bi^{3+}, Mn^{2+}.

Ions of the first group give stable waves which remain practically unchanged during polarographic analysis. There is an essentially linear relation between the wave height and the concentration for a fairly large concentration range. The calibration curve for Ag^+ is given in Fig. 1. It is of interest to note that the polarographic waves obtained when various salts of a particular ion are introduced into the fused salts lie fairly close on one straight line. As an example, we give a calibration curve for Cd^{2+} which was obtained by the use of different Cd salts. In addition, certain anions can be determined as well as cations when KNO_3 is used as the supporting electrolyte. In work carried out in conjunction with V.I.Kovalenko, the behavior of $Cr_2O_7^{2-}$ in fused KNO_3 was examined in detail. Just as for the cations, there is a linear relation between wave height and the concentration of $Cr_2O_7^{2-}$ (Fig. 3). In the course of 20-30 minutes after the addition of an aliquot of $K_2Cr_2O_7$ to the fused salt, the wave height remains almost unchanged; subsequently there is a gradual decrease as the result of a reduction process. The potentials at which ions of this group are deposited are given below.

Reduction potentials for ions using KNO_3 as supporting electrolyte at a temperature of 380-380°

Ag^+ = -0.05 V; Pb^{2+} = -0.25 V;
Cd^{2+} = -0.42 V; $Cr_2O_7^{2+}$ = -0.40 V.

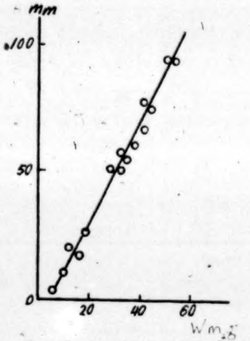


Fig. 1. Calibration curve for Ag ions using KNO_3 as the supporting electrolyte.

Determination of arbitrary amounts of the given ions by means of the calibration curves given above give completely satisfactory results (Table 1).

Ions of the second group give unstable waves which gradually decrease because of the decomposition of the nitrates according to the reaction $2Me(NO_3)_2 = 2MeO + 4NO_2 + O_2$.

The metal oxides thus formed are insoluble in KNO_3 and $NaNO_3$. For these ions, well defined polarographic waves, the height of which is proportional to concentration, are only obtained immediately after the addition of an aliquot of the respective salt to the melt. The stability of the polarographic wave can be increased by making the melts acid. If $KHSO_4$ is added to fused KNO_3 at 200-250°, then the nitrates of the ions belonging to this group will not decompose in this melt; the melt remains unchanged over a considerable time, and the wave height of the respective ions remains constant. When an acidic supporting electrolyte of this type is used, a straight line relation between wave height and concentration is found for Cu^{2+}, Ni^{2+}, Co^{2+} ions. A calibration curve for Cu^{2+} using an acidic nitrate melt as a supporting electrolyte is shown in Fig. 4 as an example. Hg^{2+} ions belong to this class of ions, which give unstable waves. In this case, however, the instability of the wave is related to the sublimation of mercury salts at the high temperatures used. The reduction potentials of the ions of this groups are as follows.

Hg^{2+} = 0; Ni^{2+} = -0.65 V;
Cu^{2+} = 0.1 V; Co^{2+} = -1.0 V.

The cobalt ion is reduced at the point where there is an increase in the current, to which the supporting electrolyte itself gives rise, so that the Co waves can only be located with great difficulty.

There is a partial drop in wave height with time for $Cr_2O_7^{2-}$ also; this occurs because of the partial decomposition of KNO_3 with time at high temperatures, according to the equation: $2KNO_3 = 2KNO_2 + O_2$.

The NO_2^- ion thus formed then reduces the $Cr_2O_7^{2-}$ ions as described below, and the wave height for Cr_2O_7 drops.

To the ions of the third group belong those ions the nitrate salts of

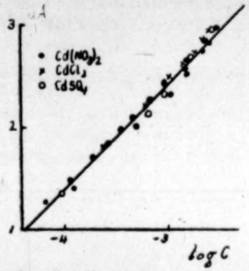


Fig. 2. Calibration curve for Cd^{2+} using KNO_3 as supporting electrolyte.

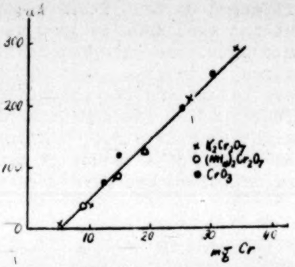


Fig. 3. Calibration curve for $Cr_2O_7^{2-}$ using KNO_3 as supporting electrolyte.

TABLE 1

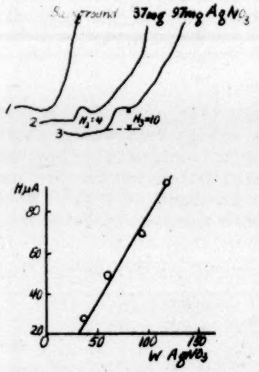
Determination of Arbitrary Amounts of Salts

						Error, %
$AgNO_3$	Taken, mg	7	21	51.5		1.2
	Found, mg	7	22	53		
$Cd(NO_3)_2$	Taken, mg	42.5	72.5	91.5	98.5	2.6
	Found, mg	44	72.5	95	100	
$Pb(NO_3)_2$	Taken, mg	36	40 53	72	90	2.5
	Found, mg	38	43 56	75	90	
$K_2Cr_2O_7$	Taken, mg		88 132	290	396	4.0
	Found, mg		85 130	300	392	

TABLE 2

Reduction Potentials for Certain Ions, Using Chlorides as Supporting Electrolytes

Ion	Temperature, (°C)	Reduction potential (V)
Bi^{3+}	460	+0.55
Cu^{2+}	445	-0.08
Ag^{2+}	360	-0.15
Ni^{2+}	480	-0.50
Cd^{2+}	700	-0.55
Co^{2+}	450	-0.54



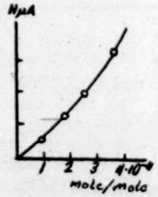


Fig. 4. Calibration curve for Cu^{2+}, using an acidic nitrate eutectic as supporting electrolyte.

Fig. 5. Current voltage curves and calibration curve for Ag, using a nitrate eutectic as supporting electrolyte, and a rotating electrode.

which decompose easily below the temperature at which polarographic determinations are carried out. These salts, on being introduced into the fused supporting electrolyte, immediately decompose with formation of the oxide of the are carried out. These salts, on being introduced into the fused supporting electrolyte, immediately decompose with formation of the oxide of the respective metal, and no polarographic wave is obtained.

Similar results can be obtained by using the rotating electrode. A current-voltage curve for Ag which was taken using a rotating electrode in a supporting electrolyte of a low melting nitrate eutectic at 250° is given in Fig. 5. It is clear from these curves that a straight line relation exists between wave height and concentration.

The characteristic behavior of certain ions in a nitrate eutectic is worth noting. Despite the good solubility and stability of zinc salts, no waves could be obtained for zinc. This is connected with the very negative potential of zinc - below -1.0 V. The zinc wave coincides with the general increase in the current-voltage curve for the supporting electrolyte, and therefore cannot be determined. No waves were obtained for thallium either, because of the insolubility of TlCl in fused KNO_3. Of special interest is the behavior of potassium chromate in the supporting electrolyte. In spite of the complete solubility of this salt, no wave could be found for CrO_4^{2-} in the electrolyte. On increasing the temperature to 500-600° a wave characteristic of sexi-valent chromium appears. On adding ammonium chromate to the supporting electrolyte the wave of sexi-valent chromium appears even at 250-300°. This phenomenon is obviously connected with the fact that potassium chromate has a very high fusion temperature ($t_{melt} = 975°$), so that at the usual temperatures for polarography in fused salts it dissolves only very slightly into ions. $(NH_4)_2CrO_4$, on the other hand, decomposes even at 180°, and thereby forms chromic anhydride, which readily dissolves in KNO_3 and gives a well defined wave.

It was thus shown that polarographic determinations employing fused nitrates as supporting electrolytes are exclusively related to the stability of the respective salts at the temperature used. For the rest, from the analytical point of view there are no differences in principle between the polarography of solutions and that of fused salts.

Fused chlorides are more interesting than fused nitrates as supporting electrolytes. However, they do possess one disadvantage - a higher melting point. Even when fused chloride eutectics are employed, the temperature has to be kept at not less than 400-450°. Since the chlorides act as a neutral supporting electrolyte and are also more thermally stable than the nitrates, practically all the ions mentioned above can be successfully determined polarographically by means of fused chlorides as the supporting electrolyte. The only restriction is the reduction potential of the ion being determined. As indicated above, ions with reduction potentials below -1 V cannot be polarographically determined in fused salts because of the general increase in the voltage-current curve for the supporting electrolyte itself, which makes interpretations of the polarograms difficult. The reduction potentials of some ions using fused chlorides as supporting electrolyte are given in Table 2. The polarographic waves obtained when chlorides are used are more stable than those obtained using nitrates. Even on long standing the wave height remains unchanged. There is a straight line relation between wave height and concentration over a considerable concentration range. Determinations of arbitrary amounts of soluble ions by means of these straight lines give completely satisfactory results.

The mean error for a determinations is 3-4%. Copper and bismuth ions give good results during quantitative determinations. Copper salts are quite volatile when chlorides are used as supporting electrolyte, as a result of which the copper wave decreases fairly rapidly with time. Bismuth chloride contains a considerable amount of oxychloride, which is insoluble in the fused chlorides.

Fused silicates were also tried as supporting electrolytes. The characteristic features of this work on fused silicates were their high melting points and

TABLE 3

Determination of Arbitrary Amounts of Ni and Co Chlorides

$NiCl_2$	Taken, mg	95	153			
	Found, mg	98	148			
$CoCl_2$	Taken, mg	69	85	106	135	156
	Found, mg	73	92	104	136	157

their corrosiveness. The dipping electrode was used only with difficulty, because the porcelain and quartz tubes used for leading in the gas were very rapidly corroded by the melts, so that the polarographic relations were distorted. The micro electrode is the most convenient for working with fused silicates. As a result of the high electrical conductivity of the silicates themselves and of the insulation, large condenser currents appear on the polarograms and cannot be completely suppressed. The polarograms have a "creeping" character, and determination of the polarographic wave is very difficult. Despite this, a linear relation can be obtained between wave height and concentration for a number of ions. As an example the straight line obtained for fused copper oxide using a silicate melt as supporting electrolyte is given in Fig. 6.

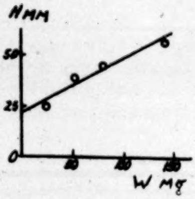


Fig. 6. Calibration curve for copper, using a silicate eutectic as supporting electrolyte.

As a result of the work carried out on the polarography of fused salts it can be seen that the polarographic determination of ions in solution in the fused salts is possible over the temperature range 180-1000°. The stability of the polarographic waves of the ions depends exclusively on the behavior of the test salt at the experimental temperature. Stable salts give well defined, stable, and easily reproducible waves. Volatile salts or ions giving unstable compounds with the supporting electrolyte give unstable waves which rapidly decrease with time. The chemical interaction between the supporting electrolyte and the ion to be determined, leading to the formation of products which are insoluble in the melt, can be prevented by making the melt acid. The order in which the ions are reduced remains basically the same as for solutions. For all the ions and for all the supporting electrolytes tested, a straight line relation was found to hold between the wave height and the concentration.

In addition to the polarographic determinations of ions, amperometric titration can also be applied for their determination in melts. Amperometric titration of ions in melts is carried out by the addition of micro amounts of the reagent which reacts with the ions to be determined. Precipitation, oxidation-reduction, and neutralization reactions, respectively, can be used for amperometric titrations just as in solution.

Precipitation reactions can be employed both for the determination of cations and anions. The alkali hydroxides can be used as universal reagents for the amperometric titrations of cations, using nitrates or chlorides as supporting electrolytes. On addition of NaOH or KOH to a melt containing some particular cation, the following reaction occurs:

$$Me(NO_3)_2 + 2KOH = MeO + 2KNO_3 + H_2O .$$

The metal oxides thus formed are insoluble in the fused chlorides or nitrates, and the wave height of the cation being determined falls. Titration can be carried out either by taking polarograms or by following the change in the diffusion current at constant potential. In the first case we get a straightened part for the equivalence point, while in the second case we get an ascending straight line. In both cases determination of the equivalence point is not difficult. This method of titration can be employed for investigating the $Cr_2O_7^{2-}$ ion by means of Ba^{2+}. The $BaCrO_4$ formed is insoluble in the fused nitrate, and the $Cr_2O_7^{2-}$ wave gradually falls. Results of titration by the precipitation method are completely satisfactory.

As an example of amperometric titration in which an oxidation-reduction reaction occuring in the melt is used as a basis, we adduce the titration of $Cr_2O_7^{2-}$ with micro amounts of $NaNO_2$, using KNO_3 as supporting electrolyte. During titration the following reaction takes place.

$$K_2Cr_2O_7 + 6NaNO_2 = 2KCrO_2 + 6NO_2 + 3Na_2O,$$

as a result of which the $Cr_2O_7^{2-}$ wave falls (Fig. 7). Determination of the equivalence point is not difficult. Titrations of arbitrary amounts of the ion to be determined, either by a precipitation reaction or by an oxidation-reduction reaction, give good results, as shown in Table 4.

TABLE 4

Determination of Arbitrary Amounts of Various Salts by Amperometric Titration

Salts	Supporting electrolyte	Result of titration					
$AgNo_3$	KNO_3	Taken, mg	53	74	75	123	144
		Found, mg	52	74	72	123	143
$CdCl_2$	KNO_3	Taken, mg	40	107	113		
		Found, mg	41	109	116		
$Pb(NO_3)_2$	KNO_3	Taken, mg	36	40	72	90	105
		Found, mg	38	43	75	90	104
$NiCl_2$	KCl + LiCl	Taken, mg	68	152	190		
		Found, mg	65	156	192		

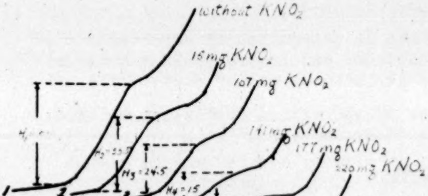


Fig. 7. Current-voltage curves for the titration of $Cr_2O_7^{2-}$ with micro-quantities of KNO_2.

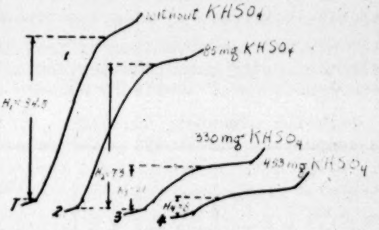


Fig. 8 Current-voltage curves for the titration of OH^- with micro-quantities of $KHSO_4$.

Amperometric titration can also be carried out on the basis of neutralization reactions. On adding alkali to a neutral melt of KNO_3 or KCl, a wave given by the hydroxyl ions is obtained, which is located at positive potentials. On adding micro amounts of $KHSO_4$ to such a fused mixture, the OH^- wave gradually decreases. The amperometric curve for such a titration is given in Fig. 8. Determination of the equivalence point is not difficult. It should be noted, however, that the concept of the precipitant for ions in solution is not the same as the concept of a precipitant for melts. Thus, in fused KNO_3, the Ag^+ ion cannot be titrated with KCl, since the AgCl dissolves readily in fused KNO_3, and no decrease in the wave height occurs. In exactly the same way the $Cr_2O_7^{2-}$ wave is not depressed on addition of Pb^{2+} to the melt. In fused silicates, amperometric titrations of cations with the universal reagent KOH cannot be carried out because the metal oxides so formed dissolve readily in the fused silicates, and free metal ions which are reduced on the solid electrode remain in the fused silicates.

The polarographic method of analyzing fused salts has great possibilities. By means of this method it is possible to follow changes in ionic concentrations which occur in the fused state. It can also be used for solving a number of physico-chemical problems relating to processes occuring in melts, the study of equilibrium between metal and melt, etc.. Of particular interest is the application of this method for investigating fused silicates, whose nature is of interest to metallurgists and geologists.

SUMMARY

1. The polarographic method of analysis using solid electrodes is a very promising method for the study of fused salts.

2. The possibility of determining a particular ion in a melt is determined fundamentally by the stability of the salt of the ion being determined polarographically at the experimental temperature.

3. The stability of a melt can be increased by making it acid by addition of $KHSO_4$.

4. Essentially linear relations were found between the wave height and concentration for the majority of ions studied.

5. Determinations of arbitrary amounts of various ions gave completely satisfactory results - the experimental error being 3-4%.

6. The concentrations of ions in melts can be determined by amperometric titration using precipitation, oxidation-reduction, and neutralization methods. Determinations of arbitrary amounts give results with errors of 3-4%.

7. The nitrates, chlorides, or silicates of the alkali metals can be used as supporting electrolytes for polarographic determinations.

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PHYSICO-CHEMICAL METHODS OF ESTIMATING ANTIBIOTICS

A COLORIMETRIC METHOD FOR THE QUANTITATIVE DETERMINATION OF STREPTOMYCIN

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The majority of chemical methods for the determination of streptomycin are based on characteristic reactions of the various functional groups in its molecule.

Thus, reactions of the carbonyl group of the streptomycin molecule are used as well as those of the guanidine group of the streptide part, and of the maltol formed from the streptose part on alkaline hydrolysis [1].

In view of the fact that preparations of streptomycin in a number of cases contain biologically inactive products of its decomposition which contain just these functional groups, and also a number of other contaminants with similar groups, the specificity of any analytical method which makes possible the determination of streptomycin alone in the presence of its decomposition products becomes of primary importance.

The simultaneous presence of guanidine and carbonyl groups in substances of biological origin is fairly rare, and the co-existence of these groups in the streptomycin molecule can therefore be used for analytical purposes. E.g., in the acridylhydrazine method of determining streptomycin, the specific properties of fluorescent streptomycin acridylhydrazine are used for its isolation from other hydrazones [2].

We have worked out a colorimetric method for the determination of streptomycin, based on the specific properties of the colored substituted hydrazone of streptomycin. As reagent we employed 2,4-dinitrophenylhydrazine, which is very widely used as a reagent in organic chemistry.

It should be noted that the given method, just like those mentioned above, is a method which determines total streptomycin and mannozide streptomycin — a substance which usually accompanies streptomycin, and which differs from streptomycin only in the presence of the _d_-mannose residue in the N-methyl-_l_-glycosamine part of the molecule. For the sake of brevity, we shall not stipulate again that in the presence of mannozide-streptomycin, both components must be determined.

During the reaction between streptomycin and 2,4-dinitrophenylhydrazine in acid media, the 2,4-dinitrophenylhydrazone of streptomycin is formed.

Excess of the colored reagent is extracted with butyl acetate. The streptomycin hydrazone remaining in the aqueous phase is colored yellow in acid solution, and the optical density _D_ in the absorption band of the solution at $\lambda = 4300$ A is a function of the streptomycin concentration.

Using highly purified streptomycin, a calibration curve _D_, _c_ was constructed, and the concentration of test solutions determined by means of it. By making up synthetic mixtures of highly purified streptomycin and glucosamine, and of streptomycin and various sugars, we showed that sugar and amino sugars do not interfere with the determination of streptomycin.

The advantage of the dinitrophenylhydrazone method is its high specificity, which enables it to be used not only for marketed streptomycin preparations, but also for the semi-products of production right up to the liquid culture stage.

EXPERIMENTAL

Two variants of the method are proposed.

First Variant. 10 ml of the solution containing streptomycin, in concentrations of from 20-120 µg/ml is introduced into a 15-20 ml test tube fitted with a ground glass stopper, and 0.5 ml of 2,4-dinitrophenylhydrazine reagent added. This reagent is prepared as follows: to 0.2 g of 2,4-dinitrophenylhydrazine - "State Chemical Reagent Purity" - are added 1 ml of concentrated sulfuric acid, 1.5 ml water, and 5 ml of rectified alcohol, and the solution thus obtained filtered if it is turbid. Fresh solution is prepared daily.

The ground glass stopper is inserted in the test tube, which is stood for 2.5 minutes in a boiling water bath; it is then removed and cooled with water. The solution is then extracted four times with approximately 10-ml portions of butyl acetate. The butyl acetate is used several times; it is purified by normal distillation. After the fourth extraction of the water phase, which is colored yellow if streptomycin hydrazone is present, it is allowed to stand, and the volume of the solution necessary to fill a 10 mm long cell taken out with a pipet. The optical density for the absorption band of the given solution $\lambda = 4300$ A is then measured on a differential photoelectric colorimeter.

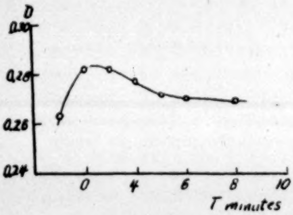

Fig.1. Relation between optical density D and the length of time for which the solutions of streptomycin and dinitrophenylhydrazine are boiled.

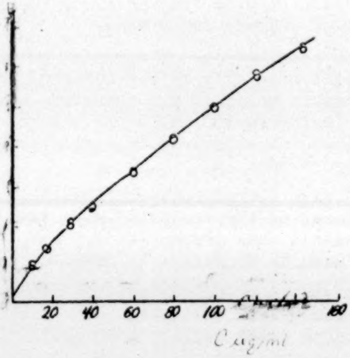

Fig. 2. Calibration curve characterizing the relation between the optical density D of streptomycin hydrazone solution and the original concentration c of the streptomycin.

When the dinitrophenylhydrazine method was carried out using water instead of the original streptomycin solution, the optical density of the aqueous phase after extraction with butyl acetate proved to be zero. We therefore used water as a comparison solution.

We studied the relation between the time of heating of the solution of streptomycin and dinitrophenylhydrazine on the optical density of the solution of streptomycin hydrazone (for $\lambda = 4300$ A).

From Fig. 1 it is clear that the maximum optical density is obtained for the hydrazone solution for a heating time of 2-3 minutes; we therefore chose a heating time of 2.5 minutes.

The calibration curve characterizing the relation between optical density D and the streptomycin concentration c was constructed, using the highly purified crystalline double salt of streptomycin hydrochloride and calcium chloride, with a known weight of streptomycin as the base.

Second Variant. Streptomycin dinitrophenylhydrazone can be formed at room temperatures and not just by boiling; at room temperature, however, the reaction is considerably slower. We determined the relation between optical density of aqueous solutions of streptomycin hydrazone and the time of standing of the solution of streptomycin plus dinitrophenylhydrazine at room temperature (Fig. 3).

It is clear from Fig. 3 that after two hours the optical density remains practically constant.

On this basis the procedure adopted for the determination of streptomycin at room temperatures is as follows: 10 ml of the original streptomycin solution is transferred to a 50-100 ml separating funnel, and 0.5 ml of the 2,4-dinitrophenylhydrazine reagent added. The solutions are well mixed and allowed to stand for 2 hours at room temperature. The solution is then extracted four times with butyl acetate, as for Variant 1. A calibration curve is constructed in the same way for this variant.

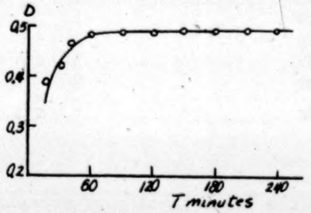

Fig. 3. Effect of time of standing of solutions of streptomycin plus dinitrophenylhydrazine on the optical density of streptomycin - hydrazone solutions.

The minimum concentration of streptomycin which can be determined (for both variants) using a 10 mm cell amounts to 15-20μ g/ml. The concentration can be lowered considerably by increasing the cell length. When a cell 40 mm long was used, it was possible to determine a streptomycin concentration of 5μ g/ml.

Both variants have a high reproducibility. The deviation between individual determinations does not exceed 2%. Determinations of streptomycin in the same sample using the two variants give the same results.

When streptomycin was determined in purified samples by the dinitrophenylhydrazone and maltol methods, coincident results were obtained. The advantage of the dinitrophenylhydrazone method as compared with the maltol method is its higher sensitivity (approximately 4-5 times).

We carried out determinations of the streptomycin content of samples of varying degrees of purity. When the streptomycin was determined in the liquid culture, protein was first of all precipitated and the culture clarified.

In order to remove proteins, we used a 15% solution of trichloracetic acid, an amount of acid being added such that its concentration in the liquid culture was finally 3%. The precipitated protein was removed by centrifuging, while the excess trichloracetic acid was extracted with benzyl alcohol [3].

The culture liquid was clarified by shaking it with 0.5% activated charcoal (calculated on the volume of the liquid) in a strongly acid medium (pH 1.5-2).

We established that at such a pH no inactivation of the streptomycin occurred in the course of 1-2 hours.

Under these conditions streptomycin is not adsorbed by the charcoal and remains completely in solution. Streptomycin can then be determined in the purified liquid culture by the usual dinitrophenylhydrazine method.

In the absence of, or for low contents of mannozostreptomycin as determined by the anthrone method [4], the streptomycin content of a sample coincides with the microbiological action of the preparation (Vide Table).

Comparison of Streptomycin Content as Determined by the Dinitrophenylhydrazine Method and from Its Microbiological Activity
(streptomycin content assumed to be 100%)

No.	Preparation	Microbiological activity, in %	Deviation between chemical and microbiological methods, in %
1	Marketed product	106	+6
2	Marketed product	103	+3
3	Marketed product	101	+1
4	Concentrate	99	-1
5	Concentrate	99	-1
6	Eluate	87	-13
7	Eluate	92	-8
8	Liquid culture	100	-0

SUMMARY

A colorimetric method has been developed for the determination of streptomycin (two variants) which has high specificity and sensitivity. By means of this method it is possible to determine streptomycin both in marketed streptomycin and in the semi-products of production right up to the liquid culture stage.

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THE SECONDARY ADSORPTION OF IONS ON ALUMINUM OXIDE ALUMINATE

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The formation of chromatograms of ions on aluminum oxide can be brought about by the following processes:

1) by adsorption of the potential-determining ions;
2) by molecular adsorption of the elctrolyte;
3) by exchange adsorption of the ions; and
4) by the precipitation of a difficultly soluble precipitate.

Ion-chromatograms on aluminum oxide aluminates [1] belong predominantly to the exchange type of chromatograms [2]. The formation of cation chromatograms on cation exchange aluminum oxide occurs as a consequence of the exchange of the cations of a solution for sodium ions [3]:

$$(Al_2O_3)_m\,AlO_2^-\,Na^+ + MZ \rightleftarrows (Al_2O_3)_m\,AlO_2^-\,M^+ + NaZ\,.$$

During the adsorption of cations on chromatographically active aluminum oxide, Schwab and coworkers discovered the phenomenon of joint adsorption of anions with multivalent cations. This phenomenon was not explained by the authors; neither was the absence of anion adsorption in the case of univalent cations taken into account.

If this fact is taken into account, the joint adsorption of anions and multivalent cations [3] can be explained as follows; part of the cations M^{2+} is exchanged with the sodium ions of the aluminum oxide aluminate, according to the scheme:

$$(Al_2O_3)_m \begin{array}{l|l} AlO_2^- & Na^+ \\ AlO_2^- & Na^+ \end{array} + MZ_2 \rightleftarrows (Al_2O_3)_m \begin{array}{l|} AlO_2^- \\ AlO_2^- \end{array} M^{2+} + 2NaZ\,,$$

while part of the cations will supercharge the aluminum oxide:

$$(Al_2O_3)_m \begin{array}{l|l} AlO_2^- & Na^+ \\ AlO_2^- & Na^+ \end{array} + \begin{array}{l} MZ_2 \\ MZ_2 \end{array} \rightleftarrows (Al_2O_3)_m \begin{array}{l|l} AlO_2^-\,M^{2+} & Z^- \\ AlO_2^-\,M^{2+} & Z^- \end{array} + 2NaZ\,.$$

On the $AlO_2^-\,M^{2+}\,Z^-$ parts, exchange of anions occurs, while the joint adsorption of anions proceeds in parallel with their absorbability on the anion exchange aluminum oxide.

During the study of the chromatographic separation of anions on anion exchange aluminum oxide aluminate, we discovered the phenomenon of the joint adsorption of cations with multivalent anions. No secondary adsorption of cations was observed in the chromatography of univalent anions.

---

1) Deceased.

By analogy with chromatography on the cation exchange aluminum oxide, the joint adsorption of cations M^+ with multivalent anions Z^{2-} on the anion exchange aluminum oxide proceeds as follows:

$$(Al_2O_3)_m\begin{array}{l:l} AlO^+ & NO_3^- \\ AlO^+ & NO_3^- \end{array} + \begin{array}{l} ZM_2 \\ ZM_2 \end{array} \rightleftarrows (Al_2O_3)_m\begin{array}{l:l} AlO^+\ Z^{2-} & M^+ \\ AlO^+\ Z^{2-} & M^+ \end{array} + 2MNO_3,$$

part of the anions is exchanged for the NO_3^- group as usual:

$$(Al_2O_3)_m\begin{array}{l:l} AlO^+ & NO_3^- \\ AlO^+ & NO_3^- \end{array} + ZM_2 \rightleftarrows (Al_2O_3)_m\begin{array}{l:l} AlO^+ & \\ & Z^{2-} + 2MNO_3 \\ AlO^+ & \end{array}$$

Consequently, the formation of secondary exchange chromatograms on anion exchange aluminum oxide is possible.

A Description Of Secondary Cation Exchange Chromatograms

Chromatographic tubes of internal diameter 0.6-1.0 cm were used for the work. Aluminum oxide aluminate was introduced into the tube in the form of a suspension in 1 N HNO_3, the column being subsequently washed with water and a solution of a mixture of 1 N salts of various elements.

1. $CuSO_4 + Cu(NO_3)_2$

The column is colored blue by the copper ions. On washing with water the lower part of the blue zone becomes white. After development with an ammonium sulfide solution the black color of the cupric sulfide only appears in the upper part of the column at the point where the blue zone was not washed with water. In accordance with the adsorption series of the anions on the anion exchange aluminum oxide [1], the SO_4^{2-} anions are found higher than the NO_3^- ions in the columns. As a result the copper ions are adsorbed only by the bivalent SO_4^{2-} ion on the anion exchange aluminum oxide; they are not adsorbed in the zone of the univalent anions of NO_3^-.

2. $NiSO_4 + Co(NO_3)_2$

Initially a rose color appears which, in accordance with the extent of washing with water, disappears. On developing with ammonium sulfide, a black zone of cobalt sulfide only appears in the upper part of the column, which indicates that the cobalt ions are only adsorbed by SO_4 ions.

3. $NiSO_4 + NiCl_2$

Initially the column is colored green by nickel ions; subsequently, on washing with water, the column becomes white. Development with ammonium sulfide shows up a black zone of nickel sulfide in the upper part of the column.

4. $UO_2(NO_3)_2 + K_2SO_4$

The column is colored yellow by uranyl ions. After washing with water the yellow color disappears, but on development with potassium ferrocyanide a red color of uranyl ferrocyanide appears.

5. $Cr_2(SO_4)_3 + UO_2(NO_3)_2 + K_2SO_4$

K_2SO_4 is added in order to increase the concentration of the sulfate ions in the solution. At the top of the column the grey-green color of chromium ions appears, while below the yellow color of the uranyl ions develops. On washing with water the gray-green color remains, while the yellow disappears, but on development with potassium ferrocyanide a red zone of uranyl ferrocyanide can be detected in the lower part.

6. $UO_2(NO_3)_2 + K_2SO_4 + CuSO_4$.

On the top a yellow zone of uranyl ions is obtained, while below the blue zone copper appears. On washing with water the yellow color disappears while the blue remains, though it gets paler. Development with ammonium sulfide gives in the upper part a brown zone of uranyl sulfide, while the bottom part becomes black with cupric sulfide.

7. $Cr_2(SO_4)_3 + CuSO_4$.

The upper part acquires the grey-green color of the chromium ions, the middle is a mixed zone, and the lower zone is blue as a result of adsorption of the copper ions. Separation of the cations is incomplete, but Cr^{3+} and Cu^{2+} form a partially mixed zone on the cation exchange column of aluminum oxide.

8. $CuSO_4 + CoSO_4$.

Two zones are formed; a blue copper zone on top and a rose cobalt zone below.

9. $CuSO_4 + NiSO_4$.

On top the blue copper zone develops, and below the green zone of nickel. On washing with water both zones become paler, particularly the nickel zone. Development with dimethylglyoxime gives a red color in the nickel zone.

10. $CoSO_4 + NiSO_4$.

One mixed zone is formed; Co^{2+} and Ni^{2+} also form a mixed zone on cation exchange aluminum oxide.

These experiments show that the formation of secondary cation exchange chromatograms on anion exchange aluminum oxide proceeds in parallel with their adsorbability on the cation exchange aluminum oxide, in the order

$$Cr^{3+} > UO_2^{2+} > Cu^{2+} > Co^{2+}, Ni^{2+}$$

(the ions separated by the comma form a mixed zone)

In conclusion, we note that when carrying out chromatographic adsorption of solutions of electrolytes it is essential to bear in mind the fact that secondary adsorption of two oppositely charged ions occurs if the adsorbed ions are multivalent.

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A VOLUMETRIC METHOD FOR THE DETERMINATION OF POTASSIUM

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In most cases potassium has to be determined in the presence of sodium, and sometimes in the presence of lithium and magnesium as well.

There are two basic methods for the determination of potassium in presence of sodium, viz., the chloroplatinate and the perchlorate methods. Both methods require a comparatively long time and require reagents which are not always readily available, or are expensive. Hitherto, no other accurate methods for the determination of potassium in the presence of sodium have been available.

Many variants of the method for the determination of potassium as the cobaltinitrite have been suggested. The chief defect of this method is that the precipitate of potassium cobaltinitrite, to which the formula $K_4Na[Co(NO_2)_6]\cdot H_4O$ is ascribed, does not always have this composition [2].

The aim of the present work was the development of a simple and rapid volumetric method for the determination of potassium, in which it is given a preliminary precipitation as potassium bitartrate. The bitartrate method is known in many variants but most research workers consider it to be insufficiently accurate. As far as accuracy is concerned it seems to us that Daubner's method [3] is the most suitable. In this method potassium is precipitated by a reagent containing 20 g of tartaric acid and 5 g sodium acetate in 1 liter of 50% aqueous alcohol.

On precipitation of the potassium bitartrate, the freed mineral acid which is formed in solution colors methyl orange a red color; $KCl + H_2C_4H_4O_6 \rightleftarrows KHC_4H_4O_6 + HCl$. According to Daubner's procedure the reagent is added until the color changes from orange to yellow. Excess of reagent should not be used, as it leads to high results.

On using the method as such, it proved to be extremely difficult to determine the necessary amount of reagent, since the change in color of the indicator for a given reagent composition is practically unobservable.

The change in color of the indicator can be made more clear cut if the ratio of tartaric acid to sodium acetate in the reagent be changed, the amount of the sodium acetate being increased. A reagent of such a composition, however, on standing deposits sodium bitartrate crystals in the form of long needles.

Another defect of this method is that sodium is introduced into the mixture being analyzed, in the reagent. This is of importance in those cases where the potassium content of a test sample is high and the determination of sodium by the uranyl acetate method is only possible after removal of the potassium [4].

We have shown that potassium can be precipitated by aniline or pyridine tartrate so that no sodium need be added. The amount of reagent necessary to precipitate the potassium is determined by the change in color of methyl orange from red to yellow. Sodium, lithium and magnesium in the form of chlorides, sulfates, or nitrates do not interfere.

To the test solution containing ca. 5 mg of K/ml, sufficient alcohol is added (methyl or ethyl) so that its final concentration in the solution is 50%. The reagent for precipitating potassium is prepared by dissolving 20 g of tartaric acid in 500 ml of water and adding 8 g of freshly distilled aniline (or 7 g of freshly distilled pyridine), and diluting to 1 liter with alcohol. The reagent is added dropwise, while the solution is continuously mixed with a glass rod. When the potassium starts to precipitate, the solution which contains methyl orange as the indicator is colored red. Mixing is continued, and more reagent added dropwise until the color of the indicator changes to yellow and does not change on adding more reagent. The potassium bitartrate which precipitates is allowed to stand for 2 hours. If on standing the solution again begins to turn red, this means that precipitation of the potassium bitartrate is still continuing and it is necessary to add further reagent till the color becomes yellow. The precipitate is filtered through a paper filter and washed four times with alcohol. The filter and precipitate are then transferred back to the beaker in which the precipitation was carried out. The precipitate is dissolved in 50 ml of hot water - 80°, which on addition of NaOH becomes colored a weak rose color when phenolphthalein is used as indicator. When the potassium bitartrate is dissolved, the rose color disappears. The solution obtained, plus the filtrate, are titrated with 0.05 N NaOH to weak rose color. 1 ml 0.05 N NaOH is equivalent to 0.00195 g potassium. It is essential that the alkali used be carbonate-free. The alkali is standardized against chemically pure KCl.

The results given in Fig. 1 are those obtained for the precipitation of potassium by aniline tartrate in the presence of sodium, lithium, and magnesium, Cl', NO_3' and SO_4'', and in Table 2 results for the precipitation of potassium with pyridine tartrate in the presence of the same ions.

TABLE 1

Precipitation of Potassium by Aniline Tartrate

Taken for analysis	Amount taken, in mg	Ml of 0.5 N NaOH used	K found, in mg	Error, in %	Amounts of other salts, in mg
KCl	25.32	12.98	25.28	-0.16	
KNO_3	23.34	11.98	23.42	+0.34	
K_2SO_4	22.40	11.48	22.44	+0.18	
KCl	33.20	17.00	33.23	+0.09	206.3 NaCl
KCl	30.05	15.33	29.97	-0.27	70.2 $MgSO_4$
KCl	35.71	18.32	35.81	+0.28	89.5 LiCl

TABLE 2

Precipitation of Potassium by Pyridine Tartrate

Taken for analysis	Amount taken, in mg	Ml of 0.5 N NaOH used	K found, in mg	Error, in %	Amounts of other salts, in mg
KCl	25.03	12.79	25.00	-0.12	
KNO_3	40.70	20.92	40.89	+0.47	
K_2SO_4	22.40	11.41	22.30	-0.45	
KCl	23.00	11.80	23.07	+0.30	171.3 NaCl
KCl	23.11	11.79	23.04	-0.26	50.3 $MgSO_4$
KCl	27.51	14.06	27.48	-0.11	40.2 LiCl

SUMMARY

1. A volumetric method for the determination of potassium by precipitation

with aniline or pyridine tartrate, respectively, has been developed.

2. The presence of sodium, lithium, magnesium, chlorine, sulfate and nitrate does not interfere.

3. For simplicity and for comparative accuracy of results, the bitartrate method is to be preferred to other methods.

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THE USE OF A COBALT CATALYST FOR THE DETERMINATION OF MANGANESE BY THE PERSULFATE METHOD

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The most widely used method for the routine analysis of manganese in various materials is that in which the manganese is first oxidized to the permanganate ion - MnO_4^-, which is then determined either colorimetrically or volumetrically. This method is universally employed and a description of it is given in many text books on analytical chemistry.

Manganese can be oxidized to the MnO_4^- ion by means of periodate, sodium bismuthate, and other strong oxidizing agents. In so far as availability is concerned, and for other reasons, the only suitable oxidizing agents in practice for large number of analyses are the persulfates, which are constantly used for this purpose.

Unfortunately, the persulfates on their own cannot oxidize the lower valency states of manganese to MnO_4^- unless silver compounds, which act as catalysts, are introduced into the solution. In order to cut down on the use of the expensive and difficultly-available silver compound, a number of methods have been described which are reported to be suitable for the oxidation of manganese, and in which only very small amounts of silver have been used [1], or silver is not employed at all [2].

Practical tests, however, showed that these methods are very unreliable in many cases, so that they have not been widely accepted in practice.

Experiments which we have carried out have shown that, for the oxidation of manganese by persulfate, it is not only silver compounds which can act as catalysts.

Cobalt compounds are very good catalysts; copper and iron compounds are not so good. This fact explains why in certain instances manganese can be oxidized even in the presence of only small amounts of silver, or sometimes even in the complete absence of silver. Oxidation occurs in these cases because the substances accidentally contain a fortuitous combination of elements which act catalytically. For other substances, however, in which the composition is different, the variants of the persulfate method suggested, in which insufficient silver is used, give completely unreliable results. The catalytic action of cobalt compounds which the authors have found is completely reliable, and enables silver compounds to be replaced in the analytical determination of manganese by the persulfate method

Cobalt Compounds As Catalysts

The oxidation of persulfates has some characteristics which will be described by the authors in detail elsewhere.

Persulfates - containing the anion $S_2O_8^{2-}$ which acts as the oxidizer - can rapidly oxidize cations, but they react only slowly with like-charged anions. Quadrivalent manganese, and even more so manganese in the higher valency states, under the experimental conditions is present in solution as the anion, and it is therefore not oxidized directly by the persulfates with sufficient rapidity. In order to achieve a rapid rate of reaction the presence of catalysts which form cations producing a strong oxidizing action is essential. The role of the catalyst thus reduces to that of an intermediate between the persulfates and the compounds of manganese being oxidized. In the case considered, therefore, the role of catalyst can be fulfilled by any element which gives rise to cations which in the lower valency states are capable of being easily oxidized by persulfates, and in the higher valency states act as strong oxidizing agents. Silver and also cobalt are suitable elements, as is apparent from the normal oxidation - reduction potential of the respective systems.

The capacity of trivalent cobalt compounds of exhibiting strong oxidizing action is well known. This is noted in analytical text books [3] and elsewhere. The reversible changes of cobalt between its different valency states occur so rapidly that a number of cobalt compounds can function as oxygen carriers, e.g., just like hemoglobin [4].

EXPERIMENTAL WORK

In the experimental work the catalytic action of cobalt was compared with that of silver, and the results obtained compared with those obtained in the absence of a catalyst. The experiments were carried out under conditions similar to those employed for the determination of manganese by the silver persulfate method.

Into a conical 250 ml flask were introduced respectively 0.002-0.01 g of manganese as a standard solution of manganese sulfate containing 0.3 mg/ml of Mn, and 15 ml of an acid mixture [600 ml dilute H_2SO_4 (1:5), 250 ml of HNO_3, sp. gr. 1.4, and 125 ml of phosphoric acid, sp.gr. 1.7]. Cobalt, iron, and the other elements or ingredients whose effect it is required to study are then added in the form of their respective solutions, and the volume finally made up to 130-150 ml with water. After the mixture has been heated to boiling, 20 ml of a 25% solution of ammonium persulfate (or 5 g of potassium persulfate) is added, after which the mixture is boiled for another two minutes. It is then cooled and after the addition of 10 ml of dilute (1:3) H_2SO_4, the permanganate formed is titrated as usual with nitrite - arsenite mixture, without the addition of NaCl. The results obtained during an investigation of the catalytic action of various elements are given in Table 1.

TABLE 1

The Catalytic Action of Various Elements

For the oxidation of Mn^{II} with ammonium persulfate in 150 ml of solution containing 5.0 mg of Mn, 0.1 mg of catalyst (calculated on the element), 15 ml of acid mixture, and 20 ml of 25% ammonium persulfate were added. The mixture was boiled for 2 minutes.

No. of expt.	Catalyst	$\%Mn^{II}$ oxidized to MnO_4^-
1	No catalyst	0
2	Ag ($AgNO_3$)	98.3
3	Co ($CoSO_4$)	100.0
4	Cu ($CuSO_4$)	60.0
5	Fe [$Fe_2(SO_4)_3$]	73.0
6	Hg ($HgCl$)($HgCl_2$)	0
7	Ni ($NiSO_4$)	0
8	Ce [$Ce_2(SO_4)_3$]	0
9	V $V_2O_2(SO_4)_2$	0
10	Mo [$(NH_4)_2MoO_4 \cdot 4MoO_3 \cdot H_2O$]	0
11	Bi $Bi(NO_3)_3$	0
12	Pb [$(CH_3COO)_2Pb$]	0

The effect of vanadium and molybdenum is interesting. These elements are not catalysts themselves, but when they are present simultaneously with cobalt, the formation of permanganate is more rapid than when cobalt alone is used.

The effect of the elements which act catalytically (Ag, Co, Cu, Fe) was also studied for various manganese contents. The results obtained, which are given in Table 2, show that it is cobalt and silver which are the best catalysts for the process.

TABLE 2

Comparative Determination of Manganese in Pure Solutions Using Various Catalysts

Volume of solution 150 ml. 0.1 mg of catalyst (calc. as the element), 15 ml of acid mixture, 20 ml of 25% ammonium persulfate are added. The mixture is boiled for 1-1.5 minutes.

Mn taken, in mg	Mn found, in mg			
	Catalyst			
	Ag	Co	Cu + Fe	Cu
1.60	1.56	1.68	1.68	0.21
2.56	2.50	2.45	2.05	1.52
3.20	3.25	3.30	2.82	2.20
4.16	4.14	4.14	4.09	–
4.80	4.77	4.60	3.18	–
6.40	6.40	6.40	–	–

Results are given in Table 3 which illustrate the effect of the presence of various elements often present in steels and cast iron on the reaction. In these cases the manganese was determined in the presence of 1 g iron, introduced into the solution as ferrous sulfate.

TABLE 3

Effect of Various Elements on the Determination of Manganese by the Cobalt-Persulfate Method

Volume of solution 150 ml. To the solution were added 1 g iron and the test element, 15 ml of the acid mixture, 3.2 mg Mn, 10 ml of 0.5% $CoSO_4 \cdot 7H_2O$ solution, and 15 ml of 25% ammonium sulfate solution. The solution was heated for 1-1.5 minutes at the boiling point.

No of expt.	Amount of element added (calcd. on the element)	Manganese	
		Amount taken, in mg	Amount found, in mg
1	None	3.2	3.19; 3.20
2	Si 5.0 mg	3.2	3.29
3	P 0.6 mg	3.2	3.29; 3.20
4	Cr 48.8 mg	3.2	3.25
5	V 1.0	3.2	3.19; 3.15
6	Mo 4.8	3.2	3.20
7	Ti 0.14	3.2	3.29
8	Ti 1.4	3.2	2.38
8-a	Ti 1.4	3.2	3.20 1)
8-b	Ti 4.2	3.2	1.5; 0.82
9	Ti 1.4 + Mo 4.8	3.2	1.14
10	Ti 1.4 + V 1.0	3.2	3.15

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1) 2 ml of $CoSO_4$ taken

From the results adduced in Table 3 it is clear that the effect of titanium is noteworthy. Under the experimental conditions, titanium apparently somehow links up with part of the cobalt (or does not succeed in oxidizing the Mn^{IV}, as a result of which all the manganese present is not oxidized to MnO_4^-. If, however, a large amount of cobalt is taken, the oxidation of the manganese proceeds normally (Table 3, experiment 8-a). In the presence of a combination of elements which accelerate the oxidation process, of perhaps paralyze the capacity of the titanium to link up with cobalt (e.g., a combination such as Ti + V), the manganese is normally oxidized even when the amount of cobalt is not increased. We also observed that a large amount of titanium hinders the determination of manganese by the usual silver - persulfate method. In order to oxidize Mn^{II} to MnO_4^- successfully, it is essential that the acidity of the solution be at a definite level, and the acid of a definite composition. This holds good to practically the same extent whether it is silver or cobalt that is used. When sulfuric acid was used alone, normal oxidation of Mn^{II} to MnO_4^-, using cobalt as a catalyst, was observed only in solutions containing not less than 10 ml of concentrated H_2SO_4 in 100 ml of the oxidizing solution. When only phosphoric acid was used, good oxidation results were not obtained, even for a phosphoric acid content of 15 ml H_3PO_4, sp.gr. 1.7, per 100 ml solution. When a mixture of H_2SO_4 and H_3PO_4 is used, it is possible to get good results over a wide acidity range. For a content of 0.7-7% H_3PO_4 (by volume for acid of sp.gr. 1.7), the concentration of H_2SO_4 can be varied between 1.5 and 3% (by volume). If the concentration of H_3PO_4 does not exceed 5% (by volume), then it is possible to use H_2SO_4 at 5% (by volume). A change in concentration of cobalt within the limits 0.7-7 ml of 0.5% $CoSO_4 \cdot 7H_2O$ / 100 ml, and possibly over an even wider range, does not affect the results.

TABLE 4

Determination of Manganese in Standary Alloys by the Cobalt-Persulfate Method

No. of expt.	Alloy	Mn content of alloy, in %	Mn determined, %			
			Catalyst			No catalyst
			Co	Co+Ni	Co+Cu	
1	Cast iron 17-c	1.57	1.60		1.62	-
2	Cast iron 63	2.41	2.40	2.44	-	-
3	Steel 20 G	0.66	0.67	0.63	0.65	-
4	Steel 118-a	0.46	0.46	0.47	0.44	-
5	Steel 150	0.83	0.83	0.80	0.81	-
6	Steel 86-a	0.48	0.50	0.49	-	-
7	Bronze 68-a	1.49	-	1.49	-	-
	Aluminum alloys					
8	Normal 69-a	0.61	0.60	0.61	0.61	-
9	Normal 72	0.33	0.35	0.35	0.33	0.30
10	Normal 74	0.22	0.23; 0.24	0.23	-	0.18
11	Normal 75	0.60	0.59	0.60	0.59; 0.60	0.43
12	Normal 76	1.00	0.99; 1.03	0.95	0.99	0.38
13	Normal 78	0.68	0.69; 0.65 0.70	1.03 -	0.67 0.68	0.28
	Alluminum alloys containing Ni and Ti (up to 0.5%)					
14	Alloy No. 21	0.44	0.45	-	-	-
15	Alloy No. 24	0.43	0.44	-	-	-
16	Alloy No. 25	0.41	0.40	-	-	-

Since cobalt compounds are easily available and difficulties crop up when certain other elements, such as titanium, are present, low concentrations of cobalt must be avoided. This is possible because for analytical purposes relatively expensive cobalt salts of high purity are not essential. Technical cobalt salts which contain Ni and Fe are completely satisfactory; of course the salts must be checked for the absence of manganese. The presence of Ni salts is even beneficial, since the green color of the nickel salts is supplementary to the rose color of the cobalt salts, and a solution containing both cobalt and nickel in the ratio 1:3 (calculated on the metals) generally appears colorless.

As indicated at the beginning of the article, in some cases when catalytically active elements are fortuitously present in the test object, manganese can be oxidized by persulfate even without the addition of a special catalyst. Naturally, results obtained in the absence of catalysts cannot be regarded as reliable.

Results for the determination of manganese in standard samples ("normals") by the procedure outlined below are given in Table 4, together with results for some of the salts when no catalyst was used.

From these results it is clear how unreliable determinations without a catalyst are.

Determination of Manganese by the Cobalt Persulfate Method

The method is applicable in those cases where the silver-persulfate can be used. Catalysts 1, 1a, and 1b act in the same way, but mixed catalysts are more convenient because they do not possess the rose color which is characteristic of solutions of cobalt salts.

Reagents Required

1) Cobalt catalyst: 0.5% solution of $CoSO_4 \cdot 7H_2O$ in water[1].

1a) Cobalt-copper catalyst: an aqueous solution containing 0.5% $CoSO_4 \cdot 7H_2O$, and 2% $CuSO_4 \cdot 5H_2O$.

1b) Cobalt-nickel catalyst: aqueous solution containing 0.5% $CoSO_4 \cdot 7H_2O$, and 1.5% $NiSO_4 \cdot 7H_2O$.

2) Acid mixture: to 600 ml of dilute H_2SO_4 (1:5) is added 250 ml HNO_3, sp. gr. 1.20, and 125 ml phosphoric acid, sp.gr. 1.7. Nitric acid, sp. gr. 1.4, is used for preparing the acid mixture for copper and aluminum alloys.

3) Ammonium persulfate - 25% solution.

4) H_2SO_4 - dilute, 1:3.

5) Standard solution of arsenite-nitrite mixture. It is standardized against a standard alloy by the method described below. Titrations can be made with either sodium arsenite or sodium thiosulfate.

Analytical Procedure

The test sample, which preferably does not contain more than 0.01 g of manganese, is dissolved in 25 ml of the acid mixture. When solution is complete, oxides of nitrogen are expelled by boiling, after which the solution is diluted with water to 150 ml. Ten ml of the catalyst solution is added and the mixture heated to boiling. 25 ml of the persulfate solution is then added carefully to the boiling solution and the whole boiled up again and the boiling maintained for 1-2 minutes, after which it is stood in a warm place until all the persulfate has decomposed. The solution is cooled in running water, and after addition of 10 ml of (1:3) H_2SO_4, it is titrated with the arsenite-nitrite mixture without addition of NaCl as is usually done when working with silver catalysts.

---

[1] Technical cobalt salts which have been checked for the absence of manganese can be used for the preparation of the cobalt catalyst, as well as cobalt compounds extracted from residues obtained during the determination of cobalt by the nitroso- β -naphthol method, electrolytically, or by other methods.

SUMMARY

Cobalt can be used as a catalyst instead of silver for the oxidation of manganese by ammonium or potassium persulfate to permanganate, which is subsequently determined colorimetrically or volumetrically.

The procedure for carrying out the oxidation and the method of determining the permanganate thus formed remains the same as when silver is used.

In view of the small amount of cobalt salt added, especially if it is added in admixture with nickel or copper, the test solution does not have the usual rose color associated with solutions of cobalt salts.

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THE DETERMINATION OF PRIMARY ALCOHOLS

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The method of estimating alcohols by acetylation with pyridine solutions of acetic anhydride has been known for a long time [1]. This method is based on the acetylation of an aliquot of the test alcohol with an accurately measured - volume or weight - amount of the acetylating agent, with subsequent determination of the excess acetic anhydride by titration.

The study which we made of this method for the determination of alcohols showed that by introducing a number of changes it is possible to increase its accuracy for primary alcohols, and to make it suitable for the determination of low molecular weight alcohols and their aqueous solutions, and also to simplify the analytical procedure.

Primary alcohols can be quantitatively acetylated in one hour at room temperature, so that the usual heating is unnecessary. This fact enables the acetylating method to be used for the determination of volatile alcohols and mixtures containing water. The accuracy of the determination depends on the accuracy with which the acetylating mixture can be measured out. For this purpose it is most convenient to use a pipet provided with a two-way tap.

During the study of the possibility of acetylating in the cold, we discovered some peculiarities in the behavior of individual alcohols. Methyl alcohol is acetylated quantitatively in 5-10 minutes; the excess acetic anhydride does not play any role. Of all the primary alcohols tested, ethyl alcohol was the most difficult to acetylate. When ethyl alcohol is being determined it is essential that the amount of acid used up in forming the ester should not be greater than 25% of the total amount. For aqueous alcohol solutions, a two-hour acetylation period is necessary; phenols are acetylated quantitatively, but also require a greater reaction time (2 hours). Primary alcohols having a double bond in the 2,3-position are acetylated at a slower rate than the saturated alcohols, so that 2 hours is also necessary for them to react completely. Secondary alcohols in pyridine at room temperature are not fully acetylated. Tertiary alcohols in general do not react, therefore the presence of tertiary alcohols does not interfere with the determination of primary alcohols.

Results for the determination of primary alcohols are given in Table 1, and for aqueous alcoholic solutions in Table 2.

EXPERIMENTAL

To an aliquot of the test alcohol weighing 0.005-0.008 mole, contained in a flask fitted with a ground glass stopper, is added, by means of a pipet with a two way tap, 3-4 ml of the acetylating mixture. The acetylating mixture is prepared by mixing one part of acetic anhydride with three parts of pyridine. After standing for one hour (or two hours for unsaturated alcohols and phenols), 20 ml of hot water is added to the contents of the flask and, after cooling, 20-25 ml of 0.5 N alkali added by means of a pipet, in order to neutralize the bulk of the acid. The rest of the acid is then titrated against the 0.5 N alkali in a buret, using phenolphthalein as an indicator.

TABLE 1

Results for the Determination of Primary Alcohols

No.	Alcohol	Found, % of that originally taken	No.	Alcohol	Found, % of that originally taken
1	Methyl alcohol	100.2	10	Octyl alcohol	99.35
2	Methyl alcohol	99.15	11	Benzyl alcohol	100.00
3	Ethyl alcohol	100.1	12	Phenylethyl alcohol	100.2
4	Ethyl alcohol	100.7	13	" "	99.97
5	Propyl alcohol	100.1	14	Cinnamic alcohol	99.2
6	Propyl alcohol	98.8	15	" "	98.8
7	Isobutyl alcohol	100.3	16	Geraniol	98.1
8	Isobutyl alcohol	100.0	17	Decanediol	98.9
9	Isoamyl alcohol (Fermentation)	98.8			

TABLE 2

Results for the Analyses of Aqueous Alcoholic Mixtures

No.	Alcohol used	Concentration, in %	
		Taken	Found
1	Methyl alcohol	50.8	51.3
2	Ethyl alcohol	18.0	18.3
3	Ethyl alcohol	49.9	49.4
4	Propyl alcohol	20.2	21.2
5	Propyl alcohol	49.9	50.9

A blank is done in exactly the same way. The differences in the titres gives the amount of alcohol present; 1 ml of 0.5 N alkali is equivalent to 0.5 millimole of alcohol.

If a volatile alcohol or mixtures containing volatile components are to be analyzed, e.g., the determination of an alcohol in ethyl acetate or chloroform, then they are introduced into a weighed, stoppered flask already containing the acetylating mixture. When mixtures containing aldehydes are titrated, the rose color tends to fade. Titration must be carried out until a stable red color is obtained.

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CRITICISM

A.A.Cherepenikov. "Handbook on the Testing and Analysis of Natural Gas", Moscow, State Geol. Press, 1951. 120 pages, 5000 copies, Price 7 rubles, 10 kopecks.

The study of natural gas is becoming of ever increasing practical importance as a result of the exceptionally rapid development of a number of branches of the national economy. Serious attention was given to the development of the gas industry in the directives of the XIX Congress of the Communist Party of the Soviet Union.

In the light of these decisions, the preparation of new cadres of gas operators, the further development of gas analysis, and the introduction into the most diverse branches of industry of basic methods for testing and analyzing gases, have become practically acute problems.

Hitherto the number of textbooks which collect together all the testing methods for gases, and can be of help to various specialists interested in this branch of knowledge has been completely insufficient. From this point of view therefore we must welcome the appearance of "Handbook on the Testing and Analysis of Natural Gas", which has been written by A.A.Cherepenikov, who can truly be considered as one of the oldest and most experienced investigators of natural gas in the Soviet Union. A large number of original articles have come from his pen in which methods for the determination of individual gases, and the natural gas resources of various regions in the USSR, have been described.

The questions dealt with in this book transcend the limits of interests of "chemists and testers working on the study of natural gas", as the author himself points out in his introduction, and should interest a wider circle of readers than A.A.Cherepenikov intends. Thus, this book will undoubtedly get attention from workers in various branches of science and practice.

The demands on books of this kind with respect to completeness are particularly high; in addition they must be completely up to date with respect to contemporary methods and techniques of gas analysis.

Unfortunately, the textbooks which have been published on this subject suffer from a number of defects which considerably lower their practical value. In this connection A.A.Cherepenikov's book is no exception.

In discussing the book's drawbacks we must first of all point out that it is not full enough. Thus, in the chapter on "Methods of Testing Natural Gas", in observing that it is essential to sweep out the apparatus with gas, the author does not indicate how much gas should be used for this purpose, and when describing the necessity of heating vessels when producing a vacuum, he does not say for how long, or at what temperature. We consider that in a textbook designed to serve as a reference book, it is not permissible to write "a tube of the respective diameter" (p. 16); "the smallest possible internal diameter" (p. 17) etc.. Similarily, in a handbook it is not usual just to mention the principle underlying some particular technique or method, as the author does in the case of an apparatus for hermetically sealing the mouth of the bore hole designed by M.N.Vorobev (p. 8), or in his description of a method of opening and sealing up vessels with "spark" gas (p. 21), and in many other places throughout the book. The description of such important apparatus as samplers should not be substituted by references to the authors' names without any indications of the literature (p. 13, et al), which incidentally appears only very seldom in the bibliography at the present time.

In the section dealing with the documentation of tests the author confines himself to listing the questions of registration cards when he should bring forward the typed form of card.

The section "Methods of Chemical Analysis of Natural Gas" also contains a number of general and indefinite instructions. E.g., "the method for the determination of H_2S by absorption in a solution of cadmium acetate and chloride, with subsequent decomposition of the cadmium sulfide formed with HCl, and iodometric titration of the H_2S evolved"' p. 37, is given without a description of the apparatus, preparation of reagents, or the necessary calculations. It is well known that the preparation of baryta water for the absorption of a small amount of CO_2 is quite complex. The author (p.8) has only this to say "all precautions should be taken to prevent the solution from coming into contact with the atmosphere". It is obvious that such instructions are not enough for the preparation of the solution. The same can be said about the preparation of palladium black (p. 6), the removal of kerosene from metallic calcium (p. 92), and the preparation of pentane baths (p. 83), etc..

There are no indications how to determine the density or the calorific value of natural gas.

Similar inaccuracies occur in many places throughout the book. The reader is compelled to look for definite answers to the practical questions brought up in A.A.Cherepenikov's book in other textbooks on various branches of knowledge. The author does not come to the reader's help in his search - there are no bibliographical references. An understanding of many of the questions relating to the apparatus is rendered difficult by the absence of the requisite diagrams and sketches. (pp. 111, 112 etc.).

The greatest drawback is the absence of a description of a large number of methods for testing and analyzing gases, which are widely used in practice but are not used by the author himself in his particular work. By confining himself to giving descriptions of only the work and apparatus used in his own laboratory, A.A.Cherepenikov in our opinion has made his book poorer than it need be. This is particularly evident in the sections dealing with the determination of individual hydrocarbons, micro and semi-micro gas analysis, and the determination of the inert gases.

Other factors which lower the practical value of the book are the smallness of the chapter devoted to "Some practical hints", and the absence of a number of essential reference tables. The material in this part of the book is completely inadequate and is of a rather haphazard character.

The experience of publishing A.A.Cherepenikov's book and also of other similar books shows that bringing out a really good handbook which gives a complete coverage of all the fundamental questions of gas technology is a particularly difficult task, and in our opinion is a problem which can only be satisfactorily solved by collaboration of a number of authors.

The obvious necessity of publishing such a book on gas analysis impels us to draw the attention of Scientific Societies to the problem of compilation and publication of such a book.

M.G.Gurevich and K.P.Florensky

November 12, 1952.

NEW REAGENTS

WATER SOLUBLE SULFONPHTHALEIN INDICATORS

New water-soluble sulfonphthalein indicators have been proposed by the Institute of Chemical Reagents for the colorimetric determination of pH.

These soluble indicators change their color for the same pH changes as the usual sulfonphthalein indicators.

No alcohol or standard alkali is necessary for the preparation of their solutions. The indicator solution is prepared by dissolving 0.1 g of the solid water soluble sulfonphthalein in 100-250 ml of distilled water.

The advantagesof these water-soluble indicators as compared to the ordinary type are obvious.

"Glavkhimreaktiv" issue the following water soluble indicators:

	pH
Thymol Blue	1.2-2.8 8.0-9.6
Bromphenol Blue	3.0-4.6
Bromcresol Purple	5.2-6.8
Bromthymol Blue	6.0-7.6
Penol Red	6.4-8.2
Cresol Red and others	7.0-8.8

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FROM THE CENTRAL COMMITTEE OF THE COMMUNIST PARTY OF THE SOVIET UNION, THE SOVIET
OF MINISTERS OF THE U.S.S.R.,
AND THE PRAESIDIUM OF THE SUPREME SOVIET OF THE U.S.S.R.

DEAR COMRADES AND FRIENDS!

The Central Committee of the Communist Party of the Soviet Union, the Soviet of Ministers of the U.S.S.R., announce to the Party and to all the workers of the Soviet Union with feelings of profound grief that on the 5th of March at 9.50 p.m., after a grievous illness Iosif Vissarionovich Stalin - Chairman of the Soviet of Ministers of the U.S.S.R. and the secretary of the Central Committee of the Communist Party of the Soviet Union - died.

Iosif Vissarionovich Stalin, the companion of Lenin and the genius who continued Lenin's work, the wise leader and teacher of the Communist Party of the Soviet Union, has died.

The name of Stalin will be forever dear to our party, to the Soviet Union, and to the workers of all the world. Together with Lenin, Comrade Stalin created the powerful party of Communists, educated and molded it; together with Lenin, Comrade Stalin was the inspirer and leader of the Great October Socialist Revolution and the founder of the first socialist state in the world. Continuing the immortal task of Lenin, Comrade Stalin led our country to a victory over fascism in the second world war, which has basically changed the international situation. Comrade Stalin has armed the party and all the nation with a great and brilliant program for the construction of communism in the U.S.S.R..

The death of Comrade Stalin, who devoted all his life to the unstinted service of the great projects of communism, is a grievous loss for the party and for the workers of the Soviet Union and of all the world.

News of Comrade Stalin's end caused the utmost grief to all the workers and intelligentsia, to all members of our glorious army, navy and air force, and to millions of workers all over the world.

In these sad days all the nation will come closer together into a large brotherly family under the experienced leadership of the Communist Party created and educated by Lenin and Stalin.

The Soviet nation has inseparable faith in, and is permeated with affection for the Communist Party of its country, since the nation knows that the supreme law which governs the activity of the party is the service of the national interests.

All workers and intelligentsia steadfastly follow the policy worked out by our party, which corresponds to the interests of the workers, and which is directed to increasing further the strength of our socialist nation. The correctness of the policy of the Communist Party has been proved in years of struggle, in which it has led the workers of the Soviet Union to the historical victory of Socialism. Inspired by this policy, the people of the Soviet Union under the leadership of the party will advance with assurance to the successful building of communism in our country.

Workers of our country know that further improvements in the material well-being of the population at all levels, workers and intelligentsia, and the greatest possible satisfaction of the material and cultural requirements of all society have been and will be the object of the special care of the Communist Party and the Soviet Government.

The Soviet nation knows that the preparedness and might of the Soviet Government increase all the time, and the party is continuously strengthening the Soviet army, navy, and air force so as to increase our readiness to deal a shattering blow to any aggressor.

The foreign policy of the Communist Party and the Soviet Government has been and will be the firm maintenance and strengthening of peace, of struggle against instigation and preparation of a new war, and a policy of international cooperation and the development of trade with all countries.

The nations of the Soviet Union under the true banners of proletairian internationalism strengthen and develop their fraternal friendship with the great Chinese nation, with the workers of all countries of the national democracies, and friendly relations with workers in the capitalist countries and the colonial countries fighting for peace, democracy, and socialism.

Dear Comrades and Friends.

The Communist Party is the great directing and leading strength of the Soviet nation in its struggle for the building of communism. The steel-like unity and the solidarity of a number of parties is the chief reason for its strength and power. We must direct ourselves to our problems - to maintain the unity of the party, to educate communists to be active political fighters for bringing to life the policies and decisions of the party, and strengthen further the links between the party and all the workers and intelligentsia, because in this direct contact with the nation lies the strength and invincibility of our party.

The party sees as one of its most important problems the education of communists and all workers in the spirit of the highest political awareness, in the spirit of an irreconcilable and firm struggle with internal and external enemies.

The Central Committee of the Communist Party of the Soviet Union, The Soviet of Ministers of the U.S.S.R. and the Praesidium of the Supreme Soviet of the U.S.S.R. turn in these sad days to the party and the nation and express their firm conviction that the party and all the workers of our country will rally even closer around the Central Committee and the Soviet Government, and will mobilize all their creative energies for the great task of building communism in our country.

The immortal name of Stalin will always live in the hearts of the Soviet people and of all progressive mankind.

Long live the great, all conquering teachings of Marx, Engels, Lenin, and Stalin. Long live our powerful socialist country. Long live our heroic Soviet nation. Long live the great Communist Party of the Soviet Union.

Central Committee of the Communist Party of the Soviet Union.	The Soviet of Ministers of the U.S.S.R.	The Praesidium of the Supreme Soviet of the U.S.S.R.

DIFFUSION OF ELECTROLYTES AND THE POLAROGRAPHIC METHOD

THE LIMITING CURRENT OF THE REDUCIBLE ION ON THE DROPPING MERCURY CATHODE

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The Ilkovich equation [1], which is the basis of quantitative polarographic analysis, is of the following form:

$$K = \frac{I_{lim}}{cm^{2/3}\,t^{1/6}} = 607 z D_{ion}^{1/2} , \qquad (1)$$

where z - is the number of Faradays of electricity required per mole of the electrode reaction; D_{ion} - is the diffusion coefficient of the ion diffusing to the electrode surface in the units $cm^2/sec.$; c - the concentration in millimols per liter; I_{lim} - the limiting diffusion current; m - the rate of flow of mercury from the capillary in mg./sec.; and t is the drop time of the mercury in seconds.

In deriving the Ilkovich equation it is assumed: 1) that there is only a radial movement of the surface of the mercury, and that there is only a symmetrical spherical diffusion to the growing drop; 2) that in the presence of a large excess of indifferent electrolyte, the limiting current of the reducible or oxidizable ion consists only of the diffusion current.

However, a study of the diffusion of electrolytes [2] under conditions approximating those which are used in polarographic analysis has shown that the limiting current of the reducible ion in the presence of a large excess of indifferent electrolyte consists of the diffusion current and a supplementary current. The latter originates in the first place as a consequence of the mixing of the liquid caused both by the tangential movement of the mercury surface and by the breaking away of the drop; secondly, by an approach to a stationary diffusion state for large drop times, and thirdly, by the fact that the transport number of the ion diffusing in excess indifferent electrolyte to the electrode surface is not equal to zero.

It has also been established that the ratio of the radius of the drop, at the moment of break away from the capillary, to the effective thickness of the diffusion layer varies from 5-13 when the drop time varies between the limits of 2-8 seconds.

The supplementary current, which is not taken into account in the Ilkovich equation, amounts to approximately 20% of the limiting current. Correct calculations of the supplementary current enable the polarographic method of analysis to be made more accurate.

The study of the effect of the concentration of the indifferent electrolyte on the limiting current, and a consideration of the effect of one ion on the limiting current of another ion when they are being determined simultaneously, is of practical interest in polarography.

Kolthoff and Lingane [3], in attempting to verify the Ilkovich equation, calculated the diffusion coefficient of an ion by means of Nernst's formula:

$$D^0_{ion} = \frac{RT}{zF^2}\lambda^0_{ion} \tag{2}$$

where D^0_{ion} – is the diffusion coefficient of an ion at infinite dilution; λ^0_{ion} – the equivalent conductivity of the ion at infinite dilution; R = 8.317 volts-coulomb/degree; F = 96,500 coulombs and T = 298°.

Equation (2) does not take into account the effect of an indifferent electrolyte on the diffusing ion and it is only valid for solutions of limiting concentration.

Kolthoff and Lingane electrolyzed Tl^+, Pb^{2+}, IO_3^- and CrO_4^{2-} in 0.1 N KCl, and having calculated the values of these diffusion coefficients by Nernst's equation, got good agreement between the observed and calculated diffusion currents. For Cd^{2+}, Cu^{2+}, Ni^{2+}, and $Fe(CN)_6^{3-}$, the deviation between the experimental results and those calculated by means of the Ilkovich equation amounts to 8%. Kolthoff and Lingane reckon that the significant deviation in the latter cases is caused by a difference in the values of the real diffusion coefficients of the ions, and the ideal values at infinite dilution.

We shall consider how much the values of the real D_{ion} differ from their ideal values.

1. Diffusion of the Salt and Diffusion of the Ion in an Indifferent Electrolyte

A knowledge of the ionic diffusion coefficients under actual experimental conditions enables one to come to a more exact interpretation of limiting currents.

By detailed investigation of the various methods of measuring diffusion coefficients, it has been established that the diffraction micro-method [4] is an exact and simple method which enables one to study the change in D of the electrolytes in relation to the concentration and influence of the indifferent electrolyte on the diffusion coefficient of the ion.

The accuracy of this diffraction method is illustrated by the results given in Table 1, in which the experimental values of the diffusion coefficients for KCl and $CaCl_2$ are compared with Harned's results [5], determined by measurements of the electrical conductivity.

TABLE 1

Differential Diffusion Coefficients of KCl and $CaCl_2$ at 25° C

Concentration, in moles per liter	$D_{KCl}\cdot10^5$ cm²/sec. Detd. by diffraction	Detd. by electrical conductivity	Diff., %	Concentration, moles per liter	$D_{CaCl_2}\cdot10^5$ cm²/sec. Detd. by diffraction	Detd. by electrical conduct.	Diff., %
0.00125	1.955	1.960	–0.3	0.001	1.270	1.248	+1.7
0.00367	1.928	1.943	–0.8	0.00133	1.250	1.225	+2.0
0.00650	1.871	1.806	+0.3	0.0030	1.210	1.199	+0.9
0.00896	1.851	1.858	–0.4	0.005	1.190	1.179	+0.1
0.0124	1.838	1.840	–0.11	0.01	1.168	–	–

The results in Table 1 show that deviations between our values and those of Harned do not exceed ± 2% The agreement in the case of KCl is better. In the case of $CaCl_2$ we observed deviations only on the positive side, apparently because of the characteristics of the electrical conductivity method.

The latter method is not applicable to the study of the diffusion coefficients of ions, since a determination of the electrical conductivity of a mixture does not enable D_{ion} to be considered. In order to compare the limiting currents obtained during the electrolysis of Cd salts in various indifferent electrolytes, with results calculated by the Ilkovich equation, we carried out a series of experiments on the determination of the diffusion coefficients of $CdCl_2$, $CdSO_4 \cdot 8/3H_2O$, and of the Cd^{2+} ions in solutions of KCl and Na_2SO_4. The results are adduced in Table 2.

From the results of Table 2 it follows that the diffusion coefficient of the salt is strongly dependent on the concentrations of the diffusing salt during which

$$D_{CdCl_2 \cdot 2H_2O} > D_{CdSO_4 \cdot 8/3 H_2O}.$$

The nature of the indifferent electrolyte has a considerable effect on the value of the ionic diffusion coefficient. The average value of $D_{Cd^{2+}}$ in 1 M Na_2SO_4 is 30% lower than the average value for $D_{Cd^{2+}}$ in 1 M KCl. The value of the diffusion coefficient of the Cd^{2+} ion in indifferent electrolytes present in large excess in the solution changes very little with an increase in concentration. E.g., for diffusion of Cd^{2+} ions in KCl, the difference between the average values of $D_{Cd^{2+}}$ and values adduced in Table 2 does not exceed +4.6-3.8%, and in the case of diffusion of Cd^{2+} in Na_2SO_4 does not exceed +2.8-2.2%.

Small deviations in the values of the diffusion coefficients of the ion from its average value lead to good results when calculating the limiting current of the reducible cation from the average value of D_{ion}.

TABLE 2

Differential Diffusion Coefficients for $CdCl_2$, $CdSO_4$, and Cd^{2+} Ions in Solutions of KCl and Na_2SO_4 at 25°C 1)

Conc. of $CdCl_2$, in moles/l	$D_{CdCl_2} \cdot 10^5$ cm²/sec.	Conc. of $CdSO_4 \cdot 8/3 H_2O$, moles/l	$D_{CdSO_4 \cdot 8/3 H_2O}$ 10^5 cm² per sec.	Conc. of Cd^{2+} diffusing in 1 M KCl	$D_{Cd^{2+}} \cdot 10^5$, cm²/sec.	Conc. of Cd^{2+} diffusing in 1 M Na_2SO_4	$D_{Cd^{2+}} \cdot 10^5$, cm²/sec.
0.001	1.022	0.001	0.916	0.004	0.546	0.0047	0.375
0.0052	0.953	0.0024	0.888	0.0185	0.529	0.0281	0.371
0.0106	0.911	0.0072	0.839	0.0230	0.0520	0.0362	0.365
0.0156	0.878	0.0121	0.789	0.0318	0.512	0.0443	0.360
0.0238	0.852	0.0211	0.761	0.059	0.502	0.059	0.357
0.0382	0.821	0.0351	0.742	Average = 0.522		Average = 0.365	
0.0590	0.791	0.059	0.719				

The values of the real and ideal ionic diffusion coefficients differ considerably from each other. Thus, the diffusion coefficient of the Cd^{2+} ions diffusing in a solution of KCl is 24% less than the $D_{Cd^{2+}}$ calculated from Nernst's equation (for infinite dilution), and in a Na_2SO_4 medium the value of the diffusion coefficient for Cd^{2+} is 49% less than the value of $D^0_{Cd^{2+}}$. Similar deviations are observed between the experimental values and those calculated from

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1) In the series of experiments the results of which are given in Table 2, the diffusion coefficients of Cd do not depend on the concentration of the indifferent electrolyte because the concentration of the latter is almost 17-250 times that of the concentration of Cd^{2+} in solution.

Nernst's equation for the diffusion coefficients of zinc and lead in KCl and KNO_3.

The concentration of the indifferent electrolyte has also a large effect on the value of the ionic diffusion coefficient. In the presence of the indifferent electrolyte the value of the diffusion coefficient of the cation decreases as compared with the value D_{ion} calculated from Nernst's equation. The decrease in the value of D_{cation} ceases when the ratio between the concentrations of the indifferent electrolyte and the test salt is greater than 20.

The results which are adduced in Table 3, illustrate the effect of the concentration of indifferent electrolyte on the value of D_{cation}. Values for the equivalent conductivities of the ions composing the salts and the transport number of Cd^{2+}, which are calculated by means of the following formulas, are also given in this table.

$$\lambda_{ion} = \frac{D_{ion} z_{ion} F^2}{RT} ; \qquad (3)$$

$$n_{Cd^{2+}} = \frac{\lambda_{Cd^{2+}}}{\lambda_{Cd^{2+}} + \lambda_{K^+} + \lambda_{Cl^-}} \qquad (4)$$

where λ_{ion} is the equivalent conductivity of the ion; $\lambda_{Cd^{2+}}$, λ_{K^+}, λ_{Cl^-} - are the equivalent conductivities of the ions at a given concentration. The remaining symbols are the same as in Equation (2). The validity of Equation (3) was proved by us during the study of the diffusion of $BaCl_2$ [4]. It was established that the Nernst equation is also applicable for moderately dilute solutions under conditions where the equivalent conductivities of the ions at infinite dilution are substituted by the conductivities at the given concentration. The diffusion coefficient of an ion determined by the diffraction micro-method in the presence of various concentrations of the same indifferent electrolyte enters into Equation (3).

The equivalent conductivities of K^+ and Cl^- were calculated from the experimental values for the diffusion coefficient of KCl [4], by means of an equation relating D_{salt} with the ionic diffusion coefficients of the ions composing the salt [4]. Since KCl is an indifferent electrolyte, the values of D_{K^+} and D_{Cl^-} and the values of the equivalent conductivities corresponding to them, decrease with increasing KCl concentration.

On addition of an indifferent electrolyte the transport number of the Cd^{2+} ion decreases by 38% as compared with $n^0_{Cd^{2+}} = 0.415$ in the absence of an indifferent electrolyte (Table 3). With increasing concentration of the latter the value of the transport number for the Cd^{2+} ion continues to decrease insifnificantly, and then remains practically constant. The data given in Table 3 show that the value of the transport number of Cd^{2+} does not approximate zero.

2. The Limiting Current of the Reducible Ion in the Presence of Excess Indifferent Salt. The Constants of the Diffusion Current, and the Supplementary Current.

Because of the considerable deviations of the real values of the ionic diffusion coefficients from their ideal values, large discrepancies are observed between the polarographic constants K_p and the constants found by measuring the diffusion of the ion in an indifferent electrolyte, K_D (Table 4).

For cations the mean deviation amounts to +23%, while for the anion it is -23% (K_D taken as 100%).

The constant of the diffusion current K_D depends - according to the Ilkovich equation - on the values of the real diffusion coefficients of the ion diffusing in an indifferent electrolyte to the surface of a growing drop of spherical form, and characterizes only the diffusion current obtained when the ion is reduced.

TABLE 3

Change in the Diffusion Coefficient of the Cd Ions and the Changes in Its Transport Number with KCl Concentration. $C_{CdCl_2} = 4 \cdot 10^{-3}M$

$D_{Cd^{2+}} \cdot 10^5$ found, in $cm^2/sec.$	$\frac{C_{KCl}}{C_{CdCl_2}}$	Calculated			
		Cd^{2+} $\Omega^{-1} \cdot cm^2/equiv.$	λK $\Omega^{-1} \cdot cm^2/equiv.$	λCl^- $\Omega^{-1} \cdot cm^2/equiv.$	$n_{Cd^{2+}}$
0.682	1	51.25	73.78	71.0	0.2615
0.658	2	49.45	72.11	68.0	0.2608
0.620	4	46.59	71.80	67.0	0.252
0.595	8	44.71	70.60	65.2	0.2477
0.552	10	41.48	69.3	63.4	0.2381
0.540	20	40.58	68.8	58.2	0.2422
0.538	40	40.43	67.9	56.1	0.246

TABLE 4

Comparison of Experimental Values for the Constants of the Diffusion Current of Certain Ions with Those Calculated from the Ilkovich Equation

Electrolysis was conducted at 25°C in the absence of oxygen in the solution. For the electrolysis of Zn and Pb the gelatine concentration did not exceed 0.001%.

Reducible salt	Indifferent Electrolyte	$m^{2/3}t^{1/6}$ $mg^{2/3}$ $sec.^{-1/2}$	$D_{ion} \cdot 10^5$ (from diffusion measurements) $cm^2/sec.$	$D^0_{ion} \cdot 10^5$ calcd. from Nernst equation, $cm^2/sec.$	K_p found polarograph., $\mu A/m\text{-}mol/l$	K_d found by diffusion $\mu A/m\text{-}mol/l$	% diff. between K_p and K_d	K_c calcd. D^0_{ion} by Nernst equation included
$CdCl_2$	1 M KCl	1.78	0.522	0.72	3.503	2.774	+26.3	3.257
$CdCl_2$	1 M KCl	1.25	0.522	0.72	3.346	2.774	+20.6	3.257
$CdCl_2$	1 M KCl	2.28	0.522	0.72	3.509	2.774	+26.5	3.257
$CdSO_4 \cdot {}^8/_3 H_2O$	1 M Na_2SO_4	1.78	0.365	0.72	2.787	2.323	+20.0	3.257
$CdSO_4 \cdot {}^8/_3 H_2O$	1 M Na_2SO_4	1.48	0.365	0.72	2.798	2.323	+30.5	3.257
$CdSO_4 \cdot {}^8/_3 H_2O$	1 M NH_4OH+ +1M $(NH_4)_2SO_4$	1.20	0.5828	0.72	3.69	2.930	+25.90	3.257
$CdCl_2$	1 M NH_4OH+ + 1 M NH_4Cl	1.234	0.591	0.72	3.738	2.952	+26.6	3.257
$Pb(NO_3)_2$	1 M KNO_3	1.85	0.682	0.98	3.827	3.160	+21.1	3.80
$Pb(NO_3)_2$	1 M KNO_3	2.28	0.682	0.98	3.851	3.160	+21.8	3.80
$Pb(NO_3)_2$	1,6NHCl	2.73	0.471	0.98	3.230	2.635	+22.6	3.80
$Pb(NO_3)_2$	1 M KOH	1.48	0.570	0.98	3.567	2.890	+23.4	3.80
$ZnCl_2$	1 M KCl	2.24	0.520	0.72	3.415	2.768	+23.4	3.257
$ZnSO_4 \cdot 7H_2O$	1 M Na_2SO_4	2.06	0.301	0.72	2.59	2.100	+23.3	3.257
KIO_3	0.1 M KNO_3	1.83	1.63(IO_3^-)	1.09	10.85[1]	14.70 for Z = 6	−26.2	12.02 for z = 6
KIO_3	0.1 M KCl	2.18	1.71(IO_3^-)	1.09	12.06	15.06 for Z = 6	−19.92	12.02 for z = 6

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1) This value holds for the concentration interval $5 \cdot 10^{-5} - 6 \cdot 10^{-3}$ M KIO_3.

The constant of the diffusion current changes according to the nature of the indifferent electrolyte, as a consequence of the change in the real D_{ion}. The smaller the value of the diffusion coefficient of the ion, the smaller K, both in the case of the diffusion current constant found by measurement of the diffusion, and in the case of the polarographic constant. E.g., K_P for the Cd^{2+} ion in 1 M Na_2SO_4 is 20.5% less than the polarographic constant for Cd^{2+} in a KCl medium. The diffusion current constant for Cd^{2+} in Na_2SO_4 solution is approximately 16% less than K_D for Cd^{2+} in KCl as the indifferent electroltye.

When the reduction potential of the cation is reached, the flow of substance to the electrode proceeds not only under the influence of symmetrical spherical diffusion, but also under the influence of the mixing of the electrolyte.

As a result the limiting current of the reducible cation is made up of a diffusion current and a supplementary current ($I_{supp.}$). For anions of the type $HPbO_2^-$, $I_{supp.}$ makes up part of the value of the limiting current.

During the reduction of anions of the type IO_3^- and BrO_3^-, part of the substance supplied by radial diffusion is separated from the effective diffusion layer and therefore the limiting current becomes less than the diffusion current I.

The values of K adduced in the last column of Table 4 are the constants of the diffusion current as a consequence of the fact that its value includes the value of the ion diffusion coefficient at infinite dilution. The ideal ionic diffusion coefficients calculated by means of Nernst's equation have the same value for varying indifferent electrolytes. This does not correspond to actual fact, since the nature and concentration of the indifferent electrolyte exert a considerable influence on the real values of D_{ion}.

As a result of the constancy of the values of the ideal diffusion coefficients, we get constant values for the arbitrary constants of the diffusion current. The latter do not reflect the actual state of things. E.g. when a solution of KCl which contains Cd^{2+} ions is electrolyzed, the constant K of the diffusion current of Cd^{2+} is 7.7% less than K_P.

During electrolysis of a solution of Na_2SO_4 containing Cd^{2+} ions, the constant of the diffusion current K is already greater by 14% than K_P found experimentally. In the case of electrolysis of 1 M Na_2SO_4 containing Zn^{2+}, the arbitrary diffusion current constant is approximately greater than the polarographic constant. Significant deviations between the calculated and experimental values for the limiting currents are observed during the electrolysis of ions of Pb, Zn and IO_3 in Na_2SO_4, $HClO_4$ or $CaCl_2$.

The coincidence between experimental and calculated values for the limiting currents of certain reducible ions in KCl media must therefore be regarded as accidental. Such a coincidence was obtained because the value of the ideal diffusion coefficient of the cations calculated by means of Nernst's equation is greater than D_{ion} for the actual experimental conditions. The enhanced value of the ideal diffusion coefficients of the cations to a certain extent compensates for the actual difference between the value of the constant found polarographically and the value of the arbitrary diffusion current constant.

Table 14 in Kolthoff and Lingane's monograph [3] (p. 90), does not confirm the validity of the numerical diffusion coefficients and the constant in the Ilkovich equation, since the values of D_{ion} calculated by means of Nernst's equation are far from being the true values of the ionic diffusion coefficients.

On studying the diffusion of ions in an indifferent electrolyte, as used in polarographic analysis, we established that on reduction of the cation, the supplementary current on an average amounts to 23% of the true diffusion current, while on reduction of an anion the diffusion current of the latter is decreased by approximately 23%.

Since in the case of the reduction of a cation on the dropping mercury electrode the supplementary current is a part of the limiting current, and the value of $I_{supp.}$ is practically the same (for capillaries with drop time of from 2-7 sec.), we can in a general sense calculate what fraction of the current of the substance arrives at the electrode surface as a result of the supplementary effects which are not taken into account in the Ilkovich equation.

Generally we can write that

$$f_{supplementary} = \frac{cD_{ion}\,\alpha}{\delta} \qquad (5)$$

where α – is an empirical factor found by measurement of the diffusion; c – the concentration in mol/ml; – the effective thickness of the diffusion layer. For cations $\alpha = 0.23$. Then the limiting current of the reducible cation can be expressed by the following formula:

$$I_{lim.} = 4\pi r^2\, zF\,\frac{cD_{ion}}{\delta}\,0.857 + 4\pi r^2 zF\,\frac{cD_{ion}}{\delta}\,0.23\cdot 0.857 =$$

$$= 4\pi r^2 zF\,\frac{cD_{ion}}{}\cdot 0.857\cdot 1.23, \qquad (6)$$

where r – is the radius of the mercury drop; 0.857 is a numerical factor obtained from the maximum and average currents. By substituting the numerical values in Equation (6), and knowing that $r = \left(\frac{3}{4\pi d}\right)^{1/3} (mt)^{1/3}$ and $= \sqrt{\frac{3}{7}Dt}$, we get a modified Ilkovich equation:

$$I_{lim.} = 744.2zcD_{ion}^{1/2}\, m^{2/3}\, t^{1/6}, \qquad (7)$$

where D_{ion} – is the real diffusion coefficient of an ion diffusing in an indifferent electrolyte, and $I_{lim.}$ is the average limiting current. The remaining legends are the same as in Equation (1). This equation is also true for complex anions with a metal as the central atom.

Equation (7) is true only when capillaries with dropping rates of 2-7 seconds are used.

For anions which are reduced on the dropping mercury electrode with a large overvoltage, such as IO_3^- and BrO_3^-, it is possible to express the average limiting current as follows.

$$I_{lim.} = 4\pi r^2 zF\frac{cD_{ion}}{\delta}\,0.857 - 4\pi r^2 zF\frac{cD_{ion}}{\delta}\cdot 0.857\cdot 0.23 = 4\pi r^2 zF\frac{cD_{ion}}{\delta}\cdot 0.857(1-0.23). \qquad (8)$$

By transforming and substituting numerical values in Equation (8), we find that:

$$I_{lim.} = 465.9\ zcD_{ion}^{1/2}\, m^{2/3}\, t^{1/6}. \qquad (9)$$

Equation (9) is approximate since the Ilkovich equation for the reduction of anions becomes less accurate for t = 3 as a result of the low value of r/δ.

In order to check the numerical constant of the modified Ilkovich Equations (7) and (9), we carried out a series of experiments on the electrolysis of various concentrations of $Cu(NO_3)_2\cdot 3H_2O$ in 1 M HNO_3, $CdSO_4\cdot {}^8/_3\,H_2O$ in

1 M NH_4OH, containing 1 M $(NH_4)_2SO_4$, and KIO_3 in 1 M KOH.

Oxygen was removed (by bubbling hydrogen) before hydrolysis of the nitric acid solutions of copper and iodate. The nitric acid solution of bivalent copper contained not more than 0.001% gelatin. Oxygen was removed from the ammoniacal solutions of $CdCl_2$ by means of sodium sulfite. The real ionic diffusion coefficients were determined in these media by means of the diffraction micromethod. The results are given in Table 5.

TABLE 5

Comparison of Experimental Values for the Limiting Current of Certain Ions with the Values Calculated by Means of Equations (7) and (9)

Reducible salt in m-mols/l	Indifferent electrolyte	Complex forming electrolyte	$D_{ion} \cdot 10^5$ cm^2/sec	m, mg/sec	t, sec.	Limiting current in μA		Diff. between exptl. and calcd. values, in %
						Found	Calcd.	
$Cu(NH_3)_2 \cdot 3H_2O$								
0.630	1 N HNO_3	-	0.472	1.59	5.28	3.61	3.66	-1.5
1.03	1 N HNO_3	-	0.472	1.59	5.28	6.04	5.99	+0.8
2.13	1 N HNO_3	-	0.472	1.59	5.28	12.25	12.38	-1.05
4.15	1 N HNO_3	-	0.472	1.59	5.28	24.62	24.12	+2.07
$CdSO_4 \cdot {}^8/_3H_2O$								
1.0	1M $(NH_4)_2SO_4$	1 M NH_4OH	0.583	0.917	5.00	4.49	4.44	+1.2
0.5	1M $(NH_4)_2SO_4$	1 M NH_4OH	0.583	0.917	5.00	2.25	2.22	+1.4
IO_3^-								
2.22	1 M KOH	-	1.63	1.98	2.48	44.98	45.48	-1.1

The results in Table 5 which show good agreement between observed and calculated values of the diffusion currents, indicate the correctness of the numerical constants of Equations (7) and (9).

By means of the modified Ilkovich equation it is possible to calculate the real ionic diffusion coefficient if z is known and the limiting current is determined experimentally.

Since it has been shown that in the case of cation reduction on the dropping mercury cathode the supplementary current amounts on an average to 23% of the diffusion current, then it is easy to calculate I_{suppl} for each actual case. A correct calculation of the supplementary current enables the effect of one ion on another during their simultaneous determination to be calculated.

For reduction of a cation:

$$K = \frac{I_{lim}}{cm^{2/3}t^{1/6}} = 744.2\ zD_{ion}^{1/2} \tag{10}$$

This constant is not a quantity which only determines the flow of substance to the electrode as a result of symmetrical spherical diffusion; it shows what part of the substance approaches the electrode surface as a result of supplementary effects. For anion reduction;

$$K = \frac{I_{lim}}{cm^{2/3}t^{1/6}} = 465.9\ zD_{ion}^{1/2} \tag{11}$$

This constant is not the diffusion current constant. It shows what part of the substance is separated from the diffusion layer because of supplementary effects which are not accounted for in the Ilkovich equation.

For anions which are reduced on the dropping mercury electrode with a large overvoltage, K is constant for a certain concentration interval. E.g., the constant for IO_3^- has practically the same value in the interval range of 0.005 to 6 m-mol/liter, but in solutions containing more than 6 m-mols/liter of IO_3^-, a considerable decrease in the value of K is observed.

Lingane and Loveridge [6] in checking Equation (1), established that the polarographic constant is not constant, but depends to a certain extent on the characteristics of the capillary. In modifying the Ilkovich formula, they introduce an empirical correction in the index of m, and propose that K be expressed by the following equation;

$$K = \frac{I_{lim}}{cm^{0.54}t^{1/6}} = 607\ zD_{ion}^{1/2} . \tag{12}$$

This equation, however, does not eliminate the difference between the polarographic constant and the diffusion current constant. If the value of the real diffusion coefficients are substituted in Equation (12), then the left hand side of the equation is not equal to the right hand side. This inequality is the consequence of the fact that the right hand side of (1) takes into account the flow of substance to the electrode as a result of symmetrical spherical diffusion only, while the limiting current on the left hand side of the equation includes the supplementary current as well as the diffusion current. Strehlow and Stackelberg [7], in considering the variability of the polarographic constant, reckon that it is caused basically by two factors which are not taken into account in the derivation of the Ilkovich equation; 1) the presence of a convection current which gives rise to the formation of maxima on the current-voltage curves (since the authors consider this effect can be diminished by addition of surface active materials, they accordingly neglect it), 2) the low value of the ratio of the drop to the effective thickness of the diffusion layer. This factor is considered in detail by Strehlow and Stackelberg.

By introducing modifications into the differential equation for symmetrical spherical diffusion, Strehlow and Stackelberg propose the following equation for the limiting current of the reducible or oxidizable ion[1]:

$$I_{lim} = 607\ zD_{ion}^{1/2}cm^{2/3}t^{1/6}(1 + AD_{ion}^{1/2}m^{-1/3}t^{1/6}), \tag{13}$$

where A = 17.

The remaining legends are the same as in Equation (1).

The constant according to Equation (13) is equal to

$$K = \frac{I_{lim}}{cm^{2/3}t^{1/6}} = 607\ zD_{ion}^{1/2}\ (1 + 17D_{ion}^{1/2}\ m^{-1/3}t^{1/6}). \tag{14}$$

In order to compare the constants calculated by means of the Strehlow-Stackelberg equation with those calculated by means of Equations (10) and (11), and with experimental results, we carried out a series of experiments on the electrolysis of various concentrations of Cd salts in two indifferent electrolytes, and of the IO_3^- ion in KNO_3 and in KOH. By substitution in Equations (10), (11), and (14) of the average values of the real diffusion coefficients, we got the results adduced in Table 6.

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[1] We shall not dwell in this paper on the intermediate stages of the mathematical solution of the modified equation for symmetrical spherical diffusion proposed by Strehlow and Stackelberg. This question will be dealt with in a separate paper.

TABLE 6

Comparison of the Values of the Experimental Constants and Those Calculated for Cd^{2+} and IO_3^- in Various Media

Reducible ion in m-mol/liter	Indifferent electrolyte	$D_{ion} \cdot 10^5$, cm²/sec.	m, mg/sec.	t, sec.	K_p, μA (experimental)	K_c, μA, from eqtns. (10), (11)	K_c, μA, from eqtn. (14)	Diff. % between K_p and K_c from eqtns. (10), (11)	Diff. % between K_p and K_c from eqtn. (14)
Cd^{2+}									
0.653	1 M KCl	0.522	0.847	7.33	3.34	3.40	2.91	-1.79	+14.7
1.635	1 M KCl	0.522	0.847	7.33	3.46	3.40	2.91	+1.60	+18.7
3.265	1 M KCl	0.522	0.847	7.33	3.46	3.40	2.91	+1.60	~ +18.8
6.530	1 M KCl	0.522	0.847	7.33	3.46	3.40	2.91	+1.60	~ +18.9
1.96	1 M KCl	0.522	1.91	2.46	3.51	3.40	2.87	+2.4	~ +22.0
5.90	1 M KCl	0.522	1.95	2.36	3.33	3.40	2.87	-2.2	+15.7
9.50	1 M KCl	0.522	1.90	2.36	3.52	3.40	2.87	+3.5	~ +22.6
29.50	1 M KCl	0.522	1.842	2.28	3.44	3.40	2.87	+1.3	~ +19.9
0.59	1 M Na_2SO_4	0.366	1.865	2.52	2.84	2.85	2.39	-0.28	+18.6
1.18	1 M Na_2SO_4	0.366	1.865	2.52	2.89	2.85	2.39	+1.60	+20.9
2.95	1 M Na_2SO_4	0.366	1.865	2.52	3.00	2.85	2.39	+5.3	+25.2
0.70	1 M Na_2SO_4	0.366	1.116	5.52	2.74	2.85	2.42	-3.96	+13.0
0.14	1 M Na_2SO_4	0.366	1.116	5.52	2.80	2.85	2.42	-1.62	+15.7
1.0	1 M Na_2SO_4	0.366	1.116	5.52	2.74	2.85	2.42	-3.90	+13.1
IO_3^-									
0.33	0.02 M KOH	1.63	1.91	2.56	11.67	11.28	15.66	+3.5	-25.48
0.33	0.1 M KNO_3	1.63	1.91	2.56	11.29	11.28	15.66	+0.1	-27.9
1.67	0.1 M KNO_3	1.63	1.91	2.56	10.92	11.28	15.66	-3.19	~ -30.26
4.17	0.1 M KNO_3	1.63	1.91	2.56	10.76	11.28	15.66	-4.6	~ -31.3

The constants calculated by means of (10), (11), and (14) are taken as 100%. The deviations between the observed values and those calculated from (10) and (11) do not exceed ±5 %.

This is because in deriving these equations the average supplementary current is used, while it is not taken into account that this current changes with the dropping rate.

The considerable deviations between the experimental values and those calculated by means of (14) are explained by the fact that the supplementary current which is included in the limiting current of the reducible ion is not accounted for in Strehlow and Stackelberg's equation. In the case of cation reduction the divergence between experimental and theoretical is positive, while for the reduction of anions it is negative.

If the values of the ideal diffusion currents calculated by means of Nernst's equation are substituted in Strehlow and Stackelberg's equation, then the values of the constants for Cd^{2+} in KCl come near to the experimental values. Nevertheless, in the case of Cd^{2+} in Na_2SO_4, just the same divergences are observed between experimental and calculated values as when the Ilkovich equation is used. E.g., it was found polarographically that $K_{Cd^{2+}} = 2.98$ μA, while the value calculated from Equation (14) is 3.36 μA (a difference of 16.3%). $D_{Cd^{2+}}$ from the Nernst equation is included in this value of the calculated constant. For other ions the constants differ to an even greater extent.

Thus, satisfactory agreement between observed and calculated values of the constants for Cd^{2+} in KCl is fortuitous, and is exclusively the result of the value of the ideal diffusion coefficient of Cd^{2+}, the magnitude of which is greater than D_{ion} for actual experiments. The enhanced value of the cationic diffusion coefficient to a certain extent compensates for the difference between K_p and the constant calculated by means of Strehlow and Stackelberg's equation.

From the results of Table 6 it follows that Equations (10) and (11) are approximate. They enable one to determine the real diffusion coefficient of the ions with an accuracy of ±5% from the value of the limiting current.

The Strehlow-Stackelberg equation, as a result of the considerable divergence between experimental and calculated results, is not suitable for calculating the limiting current of the reducible ion.

3. The Effect of the Concentration of an Indifferent Electrolyte on the Ideal Limiting Current of the Reducible Ion

It is known that, in the absence of an indifferent electrolyte, the limiting current is determined by the rate at which the reducible ions approach the electrode under the influence of electrical migration as well as of diffusion.

Kolthof and Lingane [3], taking as a basis the theory of Heyrovsky and Ilkovich re the effect of an indifferent electrolyte on the limiting current of the reducible ion, and considering that the diffusion current should change appreciably on adding an indifferent electrolyte as a result of changes in the effective diffusion coefficient of the reducible ion, proposed the following ratio between the initial limiting current in the absence of an indifferent electrolyte and the limiting diffusion current in the presence of excess indifferent electrolyte. For cation reduction:

$$\frac{I^{0}_{lim}}{I_{lim}} = \left(\frac{D_{salt}}{D_{ion}}\right)^{1/2}\left(\frac{1}{1-n^{0}_{c}}\right) \tag{15a}$$

For anion reduction:

$$\frac{I^{0}_{lim}}{I_{lim}} = \left(\frac{D_{salt}}{D_{ion}}\right)^{1/2}\left(\frac{1}{1+n_{a}}\right), \tag{15b}$$

where I^{0}_{lim} is the initial limiting current in the absence of an indifferent electrolyte, I_{lim} is the limiting current in the presence of excess indifferent electrolyte, and n^{0}_{c} and n^{0}_{a} are the transport numbers in a solution not containing an indifferent electrolyte.

MacGillavry [8], also derived the following equation for the ratio $\frac{I^{0}_{lim}}{I_{lim}}$ for cation reduction:

$$\frac{I^{0}_{lim}}{I_{lim}} = \left(1+\frac{Z_{c}}{Z_{a}}\right)^{1/2}\left(1+\frac{Z_{c}\,\delta^{0}_{c}}{Z_{a}\,\delta^{0}_{a}}\right)^{1/2}\left(\frac{\delta^{0}_{c}}{\delta_{c}}\right)^{1/2}\left(\frac{t^{0}}{t}\right)^{1/6}, \tag{16}$$

where Z_c and Z_a are the valencies of the ions of the salt the cation of which is reduced; δ^{0}_{c} and δ^{0}_{a} the mobilities of the cation and anion at infinite dilution; δ_c the mobility of the reducible cation in the presence of excess indifferent salt; t^0 and t the dropping times at constant pressure in the absence and in the presence of an indifferent electrolyte, respectively.

Since $$\delta^{o}_{ion} = \frac{\lambda^{o}_{ion}}{Z_{ion}F^2}, \qquad (17a)$$

$$\delta_c = \frac{\lambda_c}{Z_c F^2}, \qquad (17b)$$

where λ_c is the equivalent conductivity of the cation at a given concentration in the presence of excess indifferent salt; λ^{o}_{ion} the equivalent conductivity of the ion at infinite dilution and $\frac{t_0}{t}$ the correction for a change in the dropping time, which tends to unity, then MacGillavry's equation can be written in the following form:

$$\frac{I^{o}_{lim}}{I_{lim}} = \left(1 + \frac{Z_c}{Z_a}\right)^{1/2} \left(1 + \frac{\lambda^{o}_c}{\lambda^{o}_a}\right)^{1/2} \left(\frac{\lambda^{o}_c}{\lambda_c}\right)^{1/2} \qquad (18)$$

Knowing the value of the real ionic diffusion coefficients, we calculated the equivalent conductivity of Cd^{2+} and IO_3^- by means of Equation (3).

We determined the real diffusion coefficients of $CdCl_2$, $CdSO_4$, and KIO_3 by the diffraction micro-method and also electrolyzed these salts with and without an indifferent electrolyte. The results thus obtained are compared in Table 7 with the values calculated from Equations (15) and (18). The values for the real diffusion coefficients of Cd^{2+} and IO_3^- are taken from Table 4.

From Table 7 it follows that the experimental results differ appreciably from the values calculated by means of (15) and (18). If the experimental are taken as 100%, then for $CdCl_2$ the ratio of the initial limiting current to the limiting current for Cd in the presence of excess KCl differs from the calculated value by 51-67%. For the reduction of $CdSO_4$ the divergence between the experimental value of $\frac{I^{o}_{lim}}{I_{lim}}$ and the calculated value amounts to + 35%.

For the reduction of the IO_3^- ion, the divergence between experimental and calculated values is -7%.

TABLE 7

Comparison of the Initial Limiting Currents of Reducible Ions without an Indifferent Electrolyte and the Limiting Currents of the Same Ions in the Presence of Excess Indifferent Electrolyte[1)]

Reducible salt	D_{salt}, 10^5 cm^2/sec	D_{ion}, 10^5 cm/sec	λ^{o}_{ion}, cm^{-1}cm^2/equiv	λ_{Cd}, cm^{-1}cm^2/equiv	I^{o}_{lim} (μA), found	I_{lim} (μA), found	I^{o}_{lim}/I_{lim} found	Calcd from Eqtn. (15)	Calcd from Eqtn. (18)
0.00065 M $CdCl_2$	1.022	0.522A	Cd 54; Cl 76	39.23A	4.24	2.74A	1.58	2.39	2.66
0.001 M $CdSO_4 \cdot {}^8/_3 H_2O$	0.916	0.364B	SO_4 81	27.5B	7.32	3.75B	1.95	2.64	2.56
0.00033 M KIO_3	1.044	1.63C	IO_3 41 K 74	–	4.41	6.93C	0.64	0.59	

---

1) The limiting current is corrected for residual current: A = 1 M KCl; B = 1 M Na_2SO_4, C = 1 M KNO_3.

Such a considerable difference between experimental and calculated values is apparently the consequence of the fact that the Kolthof and Lingane equation does not account fully for the relation existing between the limiting current and the mobility of the reducible ion in the presence of excess indifferent salt.

Moreover, the convection transfer of substance to the electrode as a result of the self-mixing of the electrolyte is not taken into account.

The Heyrovsky-Ilkovich theory, according to which the migration current is equal to the product of the transport number of the reducible ion and the value of the initial limiting current, is the basis of the Kolthof - Lingane equation.

According to Heyrovsky and Ilkovich's hypothesis [1, 9], the value of the transport number on addition of a large excess of indifferent electrolyte approximates to zero. Experimental results show, however, that on addition of a large excess of the indifferent electrolyte, the transport number of the reducible ions is not lowered by more than 35-40% as compared with n^o_{ion} (vide Table 3).

In order to check the correctness of the Heyrovsky-Ilkovich theory re the migration current which develops on using a dropping mercury electrode, we electrolyzed a solution containing $4\cdot10^{-3}$ M $CdCl_2$, and determined the initial limiting current of the reducible Cd^{2+} ion in the absence of indifferent salt. It proved to be equal to 27.01 μA. Subsequently 0.16 m KCl containing $4\cdot10^{-3}$ M $CdCl_2$ was electrolyzed. The limiting current on addition of a large excess of indifferent electrolyte was 16.88 μA (the limiting current is corrected for residual current). From these values, $I^o_{lim}/I_{lim} = 1.6$. This value is in agreement with the value of the ratio of the limiting current for Cd^{2+} without an indifferent electrolyte to its limiting current in the presence of excess indifferent electrolyte, adduced in Table 7.

Since, according to Heyrovsky and Ilkovich's theory, the migration current is equal to

$$I_M = I^o_{lim}\, n_c \quad , \tag{19}$$

then by substituting in Equation (19) the values of $n_{Cd^{2+}}$ for $4\cdot10^{-3}$ M $CdCl_2$ from Table 3, we get.

$$I_M = 27.01\cdot0.246 = 6.645\ \mu A,$$

which amounts to 39.4% of the value of the limiting current for Cd^{2+} in the presence of indifferent electrolyte.

The value obtained for the migration current is almost double that for I_{supp}, which actually remains after addition of excess indifferent salt to the solution of the reducible cation. We established above that the supplementary current amounts to 20% of the limiting current for the cation obtained on addition of excess indifferent electrolyte.

These results show that Heyrovsky's and Ilkovich's theory re the influence of the concentration of indifferent electrolyte on the initial limiting current of the reducible cation, which is based on the assumption that the migration current decreases exclusively as the result of a rapid decrease in the transport number of the ion, is not justified.

On the basis of the results given in Table 7 it has been established that the equation of Kolthof and Lingane and MacGillavry's equation respectively are not applicable to the determination of the ratio between the limiting current without an indifferent electrolyte and the limiting current in the presence of excess indifferent electrolyte.

4. Determination of Ionic Diffusion Coefficients by Means of Solid Electrodes

In concluding this paper, we consider it necessary to discuss very briefly the work of E.M. Skobets and I.S. Kavetsky [10], which was devoted to the determination of ionic diffusion coefficients by means of solid electrodes.

The authors, who developed the method of Kolthoff and Laitinen [3], showed that by measuring the fall in the current strength on a solid electrode during the first moments after the current kick it is possible to calculate the ionic diffusion coefficients in any medium.

From the results of E.M. Skobets and I.S. Kavetsky it follows that the values of the real diffusion coefficient of Tl^+ in Cd^{2+} and Zn^{2+}, in indifferent electrolytes which are present in a large excess in the test solutions, agree with the values for ideal D_{ion} calculated from the Nernst equation. Such an agreement, however, contradicts what actually happens, since it is well known that the nature and concentration of the indifferent electrolyte exerts a considerable influence on the value of the real ionic diffusion coefficient (vide the results in Table 4).

McBain and coworkers, using the method of porous diaphragms, also showed that the diffusion coefficient of a cation is lowered in the presence of a large excess of indifferent electrolyte.

The agreement between the values of the ionic diffusion coefficients calculated by means of Nernst's equation and the experimental results of Skobets and Kavetsky indicate the considerable inaccuracy of the Kolthoff-Laitinen method.

SUMMARY

1. During a study of diffusion in solutions, the concentrations of which are similar to those employed in polarographic analysis, it has been established that the limiting current of the reducible ion in the presence of a large excess of indifferent electrolyte consists of the diffusion current and a supplementary current.

2. It has been shown that the value of the supplementary current, which is not accounted for in the Ilkovich equation, amounts on the average to 23% of the basic radial diffusion current when capillaries with drop times of from 2-7 secs. are used.

3. A modified empirical Ilkovich equation is proposed for the reduction of cations and ions of the type of $HPbO_2$

$$I_{lim} = 744.2 \cdot zcD_{ion}^{1/2} m^{2/3} t^{1/6} . \qquad (7)$$

For anions of the type IO_3^- and BrO_3^- reduced on the dropping mercury cathode with an overvoltage

$$I_{lim} = 465.9 \quad zcD_{ion}^{1/2} m^{2/3} t^{1/6} , \qquad (9)$$

Equations (7) and (9) are valid for cases where the indifferent electrolyte contains only one reducible ion and for capillaries with drop times of 2-7 seconds.

By means of Equation (7), it is possible to determine how much the value of the limiting current of the reducible ion changes as a result of a previous or subsequent discharge of another ion.

4. It has been shown that the Strehlow-Stackelbergequation is not applicable for calculating the limiting current of the reducible ion.

5. It has been shown that Heyrovsky and Ilkovich's theory re the influence of the concentration of the indifferent electrolyte on the limiting current of the reducible cation, which is based on the assumption that the migration current decreases exclusively as the result of a rapid decrease in the transport number of the ion, is not justified.

It has been established that the equation of Kolthof and Lingane and MacGillavry's equation, respectively, are not applicable for the determination of the ratio between the limiting current without an indifferent electrolyte and the limiting current in the presence of excess indifferent electrolyte.

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THE APPLICATION OF THE LIQUID INTERFEROMETER IN QUANTITATIVE ANALYSIS

IV. THE QUESTION OF BREAKS AND THE DETERMINATION OF THE NUMBER OF FRINGES BETWEEN BREAKS

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Despite the varied application of the interferometric method in different fields of analysis [1, 2], the amount of work devoted to this particular method in the U.S.S.R. is nevertheless comparatively small.

As we have shown [3], the basic difficulty in carrying out measurements using the interferometric method is the correct determination of the number of interference fringes despite the phenomenon of breaks, which is observed when trying to compensate for the difference in the optical paths of the light passing through the test substance and the material used for comparison, respectively.

Marc [4], first observed the phenomenon of "breaks" when studying colloidal solutions of dextrin, albumen, gum arabic and other materials by means of an interferometric method. Even at that time Marc suggested that the reason for breaks should be sought in the difference between the dispersion of light by pure water and by a solution.

Gans and Bose [5], gave a very detailed explanation of the cause of breaks, using as an example the determination of the refractive index of gelatin solutions. They considered that breaks are caused by the difference in dispersion of light by the dissolved substance (gelatin) and by the compensator of the apparatus. When carrying out interferometric measurements, differences in the optical paths of the light in the two cells, when the cells contain materials of different refractive indexes, are compensated for by rotation of the compensator disc until the upper and lower interference spectra are completely identical. It is obvious that compensation will not occur simultaneously for all the light rays, e.g., for the yellow, red, and blue, or white as the sum, in consequence of the difference in their wave lengths and of the difference in the dispersion of the light rays produced by the test substance and by the comparator glass.

If, for very dilute solutions, the difference in dispersion of the comparator and the dissolved substance is not very important, on increasing the concentration of the solution it can increase to such an extent that two equally black fringes, or two null positions with a difference in path of one fringe, can be observed simultaneously at the compensation point, i.e., a break develops as the result of the displacement of the null position. With further increase in the concentration being measured, this phenomenon of the displacement of the null position is again repeated after a definite number of fringes, i.e., a second break occurs, etc. As the result of this periodic displacement of the null point, the curve of the number of fringes plotted against concentration has a step-like character, with intervals of one fringe, between the steps.

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[1] Deceased.

We obtained curves of this type for solutions of HCl, NaOH [3], and also partially for solutions of hydrolyzable salts [6]. Other authors have also obtained similar curves for other compounds [7-10].

As confirmation of the fact that the reason for this phenomenon of breaks is the difference between the dispersion of light by the compensator and by the dissolved substance, we adduce as an example the quantitative ratio between the dispersion of the compensator and that of gelatin [5]. When the compensator is calibrated for different lines of monochromatic light, the differences in the optical paths of the light for any inclination of the compensator are found to be in a similar ratio to each other, viz.

$$N_{red} : N_{yellow} : N_{blue} = S_{red} : S_{yellow} : S_{blue} \qquad (1)$$

where $\underline{N}$ represents the fringes, while $\underline{S}$ is the drum reading in parts of a fringe.

If N_{yellow} is taken as unity and $\underline{S}$ is taken for any position of the drum, then the above equation will be

$$N_{red} : N_{yellow} : N_{blue} = 0.8971 : 1 : 1.221. \qquad (2)$$

If the refractive index of the gelatin is denoted by $n - n_0$, then its relation to the wave length of the light can be expressed as the dispersion of the gelatin and can be represented by $\frac{n - n_0}{\lambda}$.

The respective ratios for the gelatin will then be equal to

$$\frac{n_{red} + n_{o\ red}}{\lambda_{red}} : \frac{n_{yellow} - n_{o\ yellow}}{\lambda_{yellow}} : \frac{n_{blue} - n_{o\ blue}}{\lambda_{blue}} = 0.8917 : 1 : 1.221 \qquad (3)$$

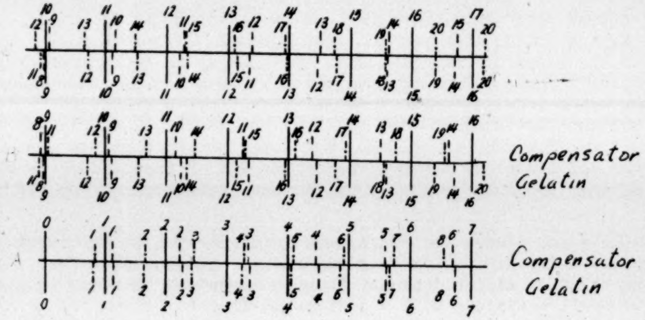

Fig. 1. Graphs A, B, C illustrating the origin of breaks as a consequence of the difference in dispersion of light by the compensator and by the solutions of the test material ---- red, —— yellow, -·-·- blue.

Three graphs are given in Fig. 1 which graphically illustrate the development of breaks as the result of the difference in dispersion of light by the comparator and by the gelatin. For greater clarity not all the rays of white light are considered - only the red, yellow, and blue waves - and they are shown on the graphs.

Analysis of graphs A and B shows that for concentrations corresponding to five spaces of the yellow fringes, the phase differences for the red and blue light in the gelatin and in the compensator are still approximately the same, but gradually increase with further increase in gelatin concentration. At a gelatin concentration corresponding roughly to the 15th yellow fringe, a fairly considerable increase in this difference occurs in the gelatin and in the compensator for the same wave lengths; this, however, disappears almost completely on shifting the compensator scale by one yellow band, as is shown graphically in Fig. 1, C.

From what has been said it follows that for interferometric measurements it is essential to take into account this phenomenon of breaks, since ignoring it leads to rather serious errors.

In previous communications [3, 6, 11], we have described the application of the interferometric method to the determination of the concentration in aqueous solutions of a number of electrolytes, including both strong (HCl and NaOH) and weak (acid and oxalic acids) types. In addition, hydrolyzable salts (Na_2CO_3 and $NaHCO_3$) have also been studied. It was shown experimentally that the measurement of the concentrations of solutions of weak electrolytes for which no breaks are observed does not present any difficulty, and the curve relating the number of bands to the concentration is a straight line. Curves of the same type for substances which exhibit breaks have a step-like shape.

It is understandable that for controlling the titers of such substances, it is first of all necessary to construct a step-like calibration curve for the concentration range in which it is proposed to take measurements, and this is a tedious operation.

In order to simplify and facilitate the work, we endeavored to find out whether or not it would be possible to construct a step-like calibration curve by determining the number of fringes between the breaks. In the course of this work preliminary measurements were made only at a few of the concentrations, instead of for all concentrations, in order to establish the initial direction of this curve.

For this purpose we made use of the following fact [5]: In principle it is possible to determine the refractive index and the dispersion of the test sample by carrying out the measurements and establishing the positions of the breaks in white light, the compensator, however, having been calibrated beforehand in monochromatic light.

Let us assume that white light consists only of yellow light of $\lambda = 587.6$ mμ and of blue light $\lambda = 486.1$ mμ. On the abscissa (Fig. 2) the number of yellow wave lengths (N_1 in the compensator and Z_1 in the dissolved material) are plotted, while the number of blue wave lengths N_2 and Z_2, corresponding to the numbers for the yellow wave lengths, are plotted on the ordinate.

Then $$N_2 = \alpha N_1 \quad (4)$$

and $$Z_2 = \beta Z_1, \quad (5)$$

where α expresses the ratio of the blue and yellow wave lengths in the compensator and equals 1.221, while β is the analogous ratio for the dissolved material.

For $N_1 = Z_1$, i.e., for an equal number of yellow wave lengths in the compensator and in the dissolved material, the number of blue wave lengths in the compensator will be less than in the dissolved material (Fig. 1). Compensation

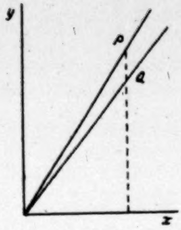

Fig. 2. Graph illustrating the difference between the number of blue waves in the compensator and in the dissolved material.

in the yellow will not lead to the same state of affairs in the blue, and the difference in the number of blue waves in the compensator and in the dissolved material will gradually increase, as shown in Fig. 2, where Q (the number of blue waves in the compensator) is lower than P (the number of blue waves in the dissolved material). On rotation of the compensator by one yellow fringe, i.e., by changing N_1 yellow to $N_1 + 1$ yellow, the number of blue wave lengths in it will become $\alpha(N_1 + 1)$. If, when this occurs, the fringes become black, then obviously the number of blue wave lengths in the compensator $= \alpha(N_1 + 1)$, which is greater than Z_2 (the number of blue wave lengths in the dissolved material) by one.

This condition can be written as follows:

$$\alpha(N_1 + 1) - 1 = Z_2$$

or

$$\alpha(N_1 + 1) - 1 = \beta Z_1, \tag{6}$$

from which $$\beta = \alpha + \frac{\alpha - 1}{Z_1}, \tag{7}$$

where β denotes $$\frac{n_{blue} - n_{o\,blue}}{\lambda_{blue}} : \frac{n_{yellow} - n_{o\,yellow}}{\lambda_{yellow}},$$

while Z_1 is the number of fringes in the interval between breaks.

From Equation (7) it follows that a knowledge of the numerical values of α and Z_1 will make it possible to calculate β, i.e., the dispersion of the dissolved material.

Further analysis of this equation leads to the prospect that if this is true for calculating β, then, naturally the reverse should also be possible; i.e., by experimentally determining α and β, it should be possible to determine Z_1, the number of fringes in the interval between breaks, which is equal to

$$Z_1 = \frac{\alpha - 1}{\beta - \alpha}. \tag{8}$$

Consequently, in order to find the value of Z_1 for the test material, it is first of all necessary to calibrate the compensator and to determine $\alpha = \frac{S_{blue}}{S_{yellow}}$, and then to determine β, which is equal to the ratio of $\frac{N}{C}$ in blue light to $\frac{N}{C}$ in the yellow.

We established above that $\beta = \frac{n_{blue} - n_{o\,blue}}{\lambda_{blue}} : \frac{n_{yellow} - n_{o\,yellow}}{\lambda_{yellow}}$

But $n_{blue} - n_{o\,blue} = \frac{N_{blue}\lambda_{blue}}{2\underline{l}}$, and $n_{yellow} - n_{o\,yellow} = \frac{N_{yellow}\lambda_{yellow}}{2\underline{l}}$

Then $$\beta = \frac{N_{blue}\lambda_{blue}}{\lambda_{blue}\,2\underline{l}} : \frac{N_{yellow}\lambda_{yellow}}{\lambda_{yellow}\,2\underline{l}} = N_{blue} : N_{yellow}. \tag{9}$$

Since the compensator of our apparatus was calibrated at the very outset of this work for the blue and green light of mercury, it was not difficult for us to calculate α for the compensator and β for the solutions of HCl, NaOH, Na_2CO_3, and $NaHCO_3$ which we measured, so that subsequently by means of the formula $Z_1 = \frac{\alpha - 1}{\beta - \alpha}$, we could calculate the number of fringes in the interval between breaks.

Below we give examples of our calculations.

I. Hydrochloric Acid

From the results of the compensator calibration it was found that [1]

$$S_{blue} = 0.073020 - 0.0000060875 \cdot x,$$
$$S_{green} = 0.057794 - 0.0000047164 \cdot x.$$

For measurements on 0.028976 N HCl, the reading on the drum in white light was $x = 399.5$ for $x_0 = 40.7$. Then

$$\alpha = \frac{S_{blue}}{S_{green}} = 1.262 \text{ and } \beta = 1.292, \text{ since } \frac{N_{blue}}{C} = 818.9 \text{ and } \frac{N_{green}}{C} = 633.7.$$

Remembering that N_{blue} and N_{green} are calculated by the formula:

$$N = \left[a + b\left(\frac{x + x_0}{2}\right)\right](x - x_0)$$ [3].

and substituting in the formula $Z_1 = \frac{\alpha - 1}{\beta - \alpha}$, the numerical values of α and β found experimentally, we find that Z_1, i.e., the number of fringes in the interval between breaks, is equal to 8.7. Actually, from measurements of solutions of HCl we found that the breaks were repeated approximately after 9 fringes, [3]

II. Sodium Hydroxide

1. For a concentration of 0.053110 M, the reading on the drum in white light was $x = 893.0$ and $x_0 = 38.13$. Then

$$\alpha = \frac{S_{blue}}{S_{green}} = 1.261 \text{ and } \beta = 1.278, \text{ since } \frac{N_{blue}}{C} = 1068.9 \text{ and } \frac{N_{green}}{C} = 836.2.$$

By means of Formula (8) we find that $Z_1 = 15.35$ fringes, which agrees with the experimental results for measurements of solutions of NaOH, for which it was found that the breaks were repeated after approximately 15 fringes [3].

2. Similarly, for $C = 0.071213$ with $x = 1197.0$ and $x_0 = 38.13$, α is again equal to 1.261. Since in this case $\frac{N_{blue}}{C} = 1069.6$ and $\frac{N_{green}}{C} = 836.9$ then $\beta = 1.278$, and accordingly $Z_1 = 15.35$ fringes.

III. Sodium Carbonate and Sodium Bicarbonate

By similar calculations it was found that for Na_2CO_3 solutions the number of fringes between successive breaks was 18-26. The experimental results in the tables [6] confirm that the first two breaks in Na_2CO_3 appear after the interval indicated. This interval increases before the appearance of the third break.

In the case of sodium bicarbonate, the periodicity of the breaks was found, by a similar method, to be 23.8 fringes, which was confirmed in practice only for the first break. The second break appears after 36 fringes [6].

It can be postulated that the anomaly in the number of breaks and the break down in the periodicity observed in the case of sodium carbonate and bicarbonate, respectively, is a direct consequence of the hydrolysis of these salts.

By similar calculations of α and β for different concentrations of oxalic and acetic acid solutions which we had investigated previously, we could find no breaks. This is in complete agreement with the experimental results of interferometric measurements [11].

Since the considerations and calculations of the values of α, β, and Z_1, adduced above for the electrolytes studied, agree with the experimental results, we may regard the problem of constructing calibration interferometric curves expressing the relation between the number of fringes and the concentration, without a preliminary determination of the concentration of the solutions throughout the required concentration range, and of carrying out the measurements in white light, to be basically solved.

It is only necessary therefore, initially, to calibrate (graduate) the compensator for two different monochromatic lines, and then by measuring a few different concentrations of the solution in white light the initial direction of the curve and the origin of the first break can be determined. Further calculations of the numerical values of α, β, and Z_1 (the number of fringes between breaks) enables the step like calibration curve to be constructed (for liquids which exhibit the phenomenon of breaks) within the concentration range of interest to the experimenter.

The construction of such a step-like calibration curve should facilitate and simplify the application of the liquid interferometer to analytical and other similar investigations.

For our measurements we used the Haber-Leve liquid interferometer. We shall not dwell on details for the calibration of the compensator and for carrying out the actual measurements, since we have done so in previous communications [3, 6, 11], and they have also been described by other authors [5, 7].

SUMMARY

1. It has been confirmed that the breaks which crop up during interferometric measurements of a number of liquids actually develop as a consequence of the difference in the dispersion of the light by the compensator of the apparatus and by the dissolved material.

2. Fundamentally the problem has been solved, and a method has been proposed for the determination of the number of fringes between breaks by a preliminary determination of the dispersion α of the compensator and the dispersion β of the dissolved substance, and by carrying out the interferometric measurements in white light.

3. A method has been suggested for constructing the step-like calibration curve for a number of substances without a preliminary determination of the concentration along the whole of the curve.

4. It has been shown that the number of fringes in the interval between the breaks has been confirmed by experimental results on the measurements of HCl, NaOH, and of hydrolyzable salts (for the first breaks) in white light.

5. The non-appearance of breaks for solutions of acetic and oxalic acids respectively has been confirmed.. This is in complete agreement with the results of interferometric measurements carried out previously.

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ANALYTICAL REACTIONS OF QUADRIVALENT VANADIUM

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Although a large amount of work has been devoted to the analytical chemistry of quinquevalent vanadium, very few analytical reactions have been described for quadrivalent vanadium. Advanced textbooks usually only mention quadrivalent vanadium compounds as reduction products of quinquevalent vanadium, or in connection with some other oxidation-reduction processes. Even the special monograph on the analytical applications of quinquevalent vanadium ("Vanadometry" [4]) devotes less than two pages to quadrivalent vanadium compounds. Meanwhile, quadrivalent vanadium compounds, which are completely stable to air, possess a number of characteristic properties which are not related at all to oxidation-reduction reactions.

These last mentioned reactions are the ones basically considered in the present article. The fact that the self-contained analytical chemistry of quadrivalent vanadium has hardly been studied at all means a serious gap in the analytical chemistry of vanadium as a whole.

In neutral and not very acid aqueous solutions, quadrivalent vanadium is present in the form of the so-called vanadyl or bivanadyl salts, containing VO^{2+} or $(VO)_2{}^{4+}$. The formal potential V^5/V^4 is equal to 1.01 volt (1.14) which indicates that the vanadyl salts are stable enought to oxidation by aerial oxygen. In acid solution they have less tendency to oxidize than, e.g., mercurous and ferrous salts.

Atomic Groups Which Are Characteristic to Reagents Which React With Quadrivalent Vanadium

On the basis of the information given below and that available in the literature, it is possible to draw the following conclusions:

In aqueous solutions V^4 reacts easily to form the combination V^4–O. Accordingly V^4 reacts with various reagents which embody salt- or complexing atomic groups which contain oxygen.

The formation of simple, individual combinations of V^4–S in aqueous media is not very characteristic; some more complicated combinations which include the V^4–S grouping are formed more easily.

The formation of the combination V^4–N (amine) in aqueous media is also not very characteristic. Such combinations are easily hydrolyzed and are transformed into the more stable V^4–O. Complex combinations which include the simple combination V^4–N are far more stable. Some of the atomic groups, viz., those groups which are characteristic of reagents giving color reactions with V^4, have been described previously [2].

In addition to supplementing the reactions dealt with previously, we give below a fuller review of atomic groups, the presence of which in the reagent molecules determines the capacity of the reagent to react readily with quadrivalent vanadium in aqueous solutions.

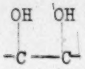
Oxygen-containing compounds

$-OH$ (I)

$-COOH$ (II)

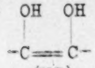
$-AsO_3H_2$ (III)

$-SeOOH$ (IV)



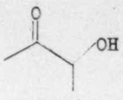
$-\overset{OH}{\overset{|}{C}}-\overset{OH}{\overset{|}{C}}-$

(V)



$-\overset{OH}{\overset{|}{C}}=\overset{OH}{\overset{|}{C}}-$

(VI)



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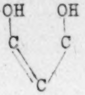

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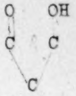
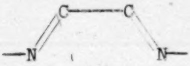


(IX)

Nitrogen-containing compounds

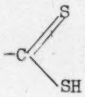


(X)

Sulfur-containing compounds

$-SH$

(XI)



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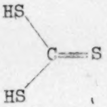
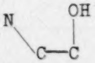


(XIII)

Mixed groupings



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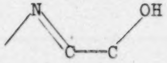

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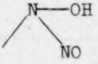

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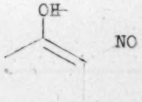

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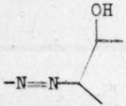

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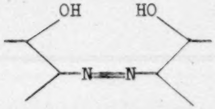
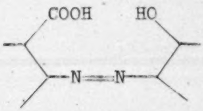


(XIX)



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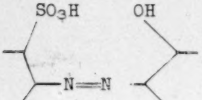
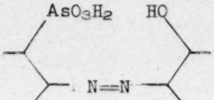
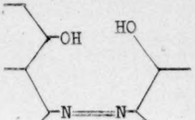


(XXI)


AsO3H2
HO
N
N

(XXII)



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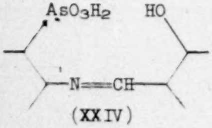
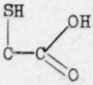

AsO3H2
HO
N
CH

(XXIV)



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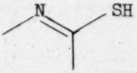

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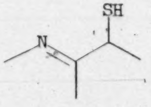

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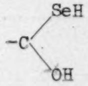


(XXVIII)

Color Reactions of Quadrivalent Vanadium

Since the color reactions of quadrivalent vanadium have already been considered [2], we shall only adduce a few more additional cases in the present article.

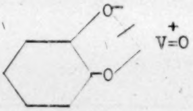
Solutions of the normal vanadyl salts have a blue color which is 5 times more intense, and is somewhat bluer in color than that of copper solutions of equivalent concentrations. It has been recommended [11], that this characteristic blue color of vanadyl salts be used for the colorimetric determination of vanadium. The color is observable in a test tube even for a concentration of 0.1 mg/ml of V^4.

The color reactions of quadrivalent vanadium may be considered to be determined by either: a) the chromophoric action of vanadium; or, b) by the ionic state of the molecules of the colored reagents.

The combination V^4–O exhibits chromophoric action, but the intense color is not, however, observed for all compounds which contain the group.

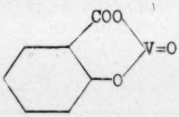
With the development of our ideas about the intramolecular dissociation of cyclic salts[3], it has now become clear that the intense color is developed with non-colored reagents in which the atom of vanadium forming the link V^4–O, or some other atom which is closely disposed to this link, is present in the ionic state. In the absence of this ionic state the color is of low intensity.

On this basis the differences in structure between the intensely colored cyclic salt of quadrivalent vanadium with pyrocatechol and the pale-colored salt formed with salicylic acid can be represented as follows1):



(I)

Intramolecular ionic
state; intense color.



(II)

No ionic state;
color not intense.

The presence of the strongly-manifested ionic state in salt (I), and its weak manifestation in (II) can be shown quite easily experimentally by means of the diazonium salts, using the method described previously[3].

Vanadium has a bond of this type in the cyclic salts of vanadium formed with the azo derivatives of pyrocatechol and salicylic acid.

The colors of the solutions formed during the color reactions of quadrivalent vanadium carried out with colored reagents are intermediate between the colors of the reagents in acid and in alkaline media. Examples of this type of reaction have been given before [2], and are also included in Table 1.

The effect of pH on the color of solutions of compounds formed during the color reactions of quadrivalent vanadium with colored and colorless reagents is not an exception to the usual rules considered elsewhere [3].

A Review of Analytical Reactions of Quadrivalent Vanadium Which Are Unrelated to Oxidation Reduction Processes

---

1) In the absence of accurate results for the composition of these salts, these structures must be considered as schematic and only emphasize the character of the bond, and not the composition of the salt.

The reactions which are described below were carried out with a solution of $VOCl_2$ prepared by the reduction of an acidified solution of sodium vanadate with the requisite amount of hydroxylamine hydrochloride and heating to the boil1). The blue solution prepared contained 10 mg/ml of V^4, ca. 50 mg HCl, and possibly a very small amount of excess hydroxylamine, which has no effect on the qualitative reactions carried out. For carrying out the reactions the solution is diluted 2 to 3 or more times with water.

For carrying out the reactions described below, a solution of the test reagent (1-2 ml) is added to 3 ml of the V^4 solution; if no outward effect is observed, 0.5 ml of 25% sodium acetate solution or 20% urotropine solution is added dropwise to increase the pH. Urotropine, if added in excess, will itself form with V^4 an almost white precipitate. The urotropine must therefore be added in amounts which are insufficient to lead to the formation of a precipitate with V^4.

Below we give a list of the reagents, together with a brief description of the outward effects observed.

1. Precipitants of Quadrivalent Vanadium

a) Inorganic

1. NH_4OH	Brown precipitate.
2, 3 NaF, Na_2SeO_3	White precipitate formed even in weak mineral acid media.
4. K_2CrO_4	On addition of K_2CrO_4 to an acid solution of V^4 and subsequent addition of urotropine, a yellow-brown precipitate is formed.
5. NH_4VO_3	Black precipitate.
6. Na_2WO_4	Dirty yellow precipitate.

b) Organic

7. Tannin	Blue precipitate. Sensitivity of the reaction 1 μg V^4/ml.
8. $K_4Fe(CN)_6$	Greenish-yellow flocculent precipitate, observable even at a V^4 concentration of 6 μg/ml.
9-13. Urotropine, phenylhydrazine, pyridine, α-aminopyridine.	Light brown, almost white precipitates, which on heating change into a greyish brown. The browning is less with phenylhydrazine than with urotropine.
14. 8-Hydroxyquinoline	On addition to an acid solution of sodium acetate a dirty yellow precipitate is formed. No precipitate is formed in acid media.
15. 8-Hydroxyquinoline	On addition of acetate a dirty yellow precipitate forms which can be observed even at a V^4 concentration of only 2 μg/ml.

---

1) 1.15 g of NH_4VO_3 is covered with 10 ml water, and 1.5 ml of 30% NaOH added to convert it into the more soluble sodium salt. The solution is evaporated to dryness. To the residue dissolved in 40 ml of water is added 10 ml of HCl (Sp. gr. 1.12) and 4 ml of a 20% aqueous solution of hydroxylamine hydrochloride, and the whole boiled for 20-30 minutes. The blue solution formed is made up to 50 ml with water. The solution contains 10 mg V^4/ml and ca. 50 mg HCl.

16. Quinaldinic acid.	Bright yellow precipitate, observable at a concentration of V^4 of 3μg/ml.
17. Cupferron	Grey precipitate observed at concentrations of V^4 of 20μg/ml. Complete precipitation for an acidity of 0.35-1μg H_2SO_4 in 200 ml [9].
18. Thionalide	White precipitate.
19. Potassium-xanthogenate	Green precipitate, which on addition of sodium acetate turns a yellow-green.
20. Sodium diethyldithiocarbamate	A yellow-brown precipitate, observable at a concentration of V^4 of 0.5μ g/ml. It can be extracted by means of organic solvents.
21. Phenylarsonic acid	In a narrow pH range a pale blue precipitate is formed which dissolves easily on acidification, or on addition of ammonia.
22. Anthraquinone-α-arsonic acid, NH_4 salt.	Grey precipitate, soluble in ammonia.

II. Precipitants Which Form Precipitates Which Dissolve On Addition of Excess Reagent

a) Inorganic

23-27. KOH, NaOH, K_2CO_3, Na_2CO_3, Na_2S	Brown precipitates which dissolve in excess reagent to give a brown colored solution.
28. $(NH_4)_2CO_3$	Grey precipitate which dissolves in a large excess of reagent.
29-32. Na_2HPO_4, $Na_4P_2O_7$, Na_2HPO_3, Na_2HAsO_4	Bluish white precipitate which is soluble in excess reagent to give a green colored solution.
33. Sodiumpolysulfides	Yellow-brown precipitate which dissolves in excess reagent to give a yellow colored solution.
34. $KBrO_3$	On addition to a non-acid solution of V^4, a yellow precipitate is formed, which is partially soluble in excess reagent.

b) Organic

35. KCN	Light green precipitate which dissolves in excess KCN to give a green colored solution.
36. Ethylenediamine	Brown precipitate which dissolves only with difficulty in excess reagent to give a yellow-brown colored solution.
37. Triethanolamine	Grey precipitate which dissolves only with difficulty in excess reagent to give a dull, lilac-grey colored solution.
38. Thiosalicylic acid	Light greenish precipitate which partially dissolves in excess reagent to give a bright green colored solution.

III. Color Reactions

a) Color reactions with colorless reagents

Clear precipitates are formed (suspensions)

7. Tannin	Blue precipitate. Sensitivity $1 \mu g\ V^4/ml$.
27. Na_2S	Brown precipitate which is soluble in excess reagent to give brown colored solutions.
19. Potassium-xanthogenate	Gives a green precipitate in acid solutions, which on addition of sodium acetate, changes to yellow-green. The precipitate can be extracted with organic solvents.
20. Sodium di-ethyl-dithio-carbamate	Yellow-brown precipitate observable at concentrations of $0.5 \mu g\ V^4/ml$. Can be extracted with organic solvents.
34. $KBrO_3$	On addition to non-acid solutions of V^4, a yellow precipitate is formed which is partially insoluble in excess reagent.
6. Na_2WO_4	Dirty-yellow precipitate.

Colored solutions (or very fine suspensions)

39. H_2O_2	Solution colored red, when excess H_2O_2 is added it becomes yellow. The reaction is similar to the reaction of H_2O_2 with quinquevalent vanadium.
40. Na_2CS_3	In weak acid media at a certain pH it goes a dark brown color. The reagent alone under these conditions gives a yellow solution, which rapidly becomes turbid.
5. NH_4VO_3	Black precipitate. In dilute solutions rose, violet, or grey colors are produced, the shade of which depends on the pH and the ratio V^4/V^5. For methods of carrying out this reaction vide [2].
41. Na_2MoO_4	In weak acid media gives colors whose shades depend on the pH. In more acid media, the color is a grey-blue, while in less acid media the color is a grey-olive.
42-44. $(NH_4)_2C_2O_4$, ammonium anthranilate, KCNS	For a concentration of ~1.5-2% of the reagent, the original blue color of the vanadium salt becomes ca. 4 times more intense, and the shade changes somewhat 1).
45. Potassium malonate	A lilac-blue color which is 2-3 times more intense than the original color of the solution 1).
46. Potassium citrate	Blue-violet color, ca. 3 times more intense than the original color of the $VOCl_2$ solution 1).
47. Ascorbic acid	Blue-green color, 2-3 times more intense than the color of the original solution. On increasing the pH the intensity diminishes.

---

1) The increase in intensity of the color is apparently connected with the formation of soluble complexes. We did not investigate by how much it would be possible to increase the sensitivity of the reaction by changing the dielectric constant of the media by adding organic solvents, (alcohol, acetone), or by the addition of salts.

48, 49. Pyrogallol, gallic acid	Do not react in acid media. On addition of sodium acetate give a very intense black-blue color which becomes blue-black on addition of ammonia (a very sensitive reaction).
50. Pyrocatechol	Acts like pyrogallol, but the color is dark blue. Sensitivity $0.5\,\mu g\ V^4$/ml.
51. 1,2-Dihydroxynaphthalene	Blue-green color after addition of sodium acetate.
52. Salicylaldehyde	On addition of sodium acetate gives an intense yellow color.

TABLE 1

b) Color Reactions with Colored Organic Reagents.

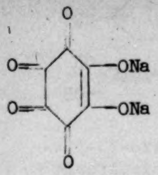
The structural formulas of these reagents are given in succeeding pages under their respective numbers.

Reagent No.	Group No.	Reagent	Color of solution under the experimental conditions.		Observations
			Reagent alone	Reagent $+V^4$	
53	VI	Sodium rhodizonate	yellow	yellow-green	
54		Picric acid	yellow	brown	sodium acetate and ammonia added dropwise
55	VII	Chloranilic acid	light-rose	brown	
56	XVII	α-Nitroso-β-naphthol	yellow	turbid brown	
57	XVII	β-Nitroso-α-naphthol	yellow	turbid red-brown	
58	XVII	Nitroso-R-salt	light-yellow	orange-brown	
59	IX	1-Hydroxyanthraquinone-4-sulfonic acid	yellow	dark orange	
60	IX, VI	Alizarin-S	orange	brownish-red	
61	IX	1,4-Dihydroxyanthraquinone-2-sulfonic acid	yellow	violet	
62	IX	1,5-Dihydroxyanthraquinone-2,6-disulfonic acid	yellow	bluish-rose	
63	IX	Carminic acid	rose	reddish-violet	An alkaline solution of the reagent is acidified with CH_3COOH, the V^4 is added, and then sodium acetate added
64	VIII, IX	Aluminon	almost colorless	turbid raspberry	
65	VIII, IX	Eriochromecyanine-R	rose	bright violet, then turbid violet	

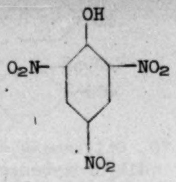
TABLE 1 (Contd.)

Reagent No.	Group No.	Reagent	Color of solution under the experimental conditions		Observations
			Reagent alone	Reagent $+V^4$	
66	VI	Gallocyanine a) weak acid media b) ammoniacal media	 rose blue	 violet almost colorless, slightly brown	 Redox reaction
67	XV	Ferron	yellow	pale greenish	Blocking reaction
68	VI	3,4-Dihydroxy-4'-nitroazobenzene-2'-sulfonic acid	yellow	brown-rose	
69	VI	3,4-Dihydroxy-naphthalene-⟨1-azo-1⟩- benzene-4- sulfonic acid	yellow	bright-rose	
70	VI	Stilbene-4,4'-bis [⟨-azo-1⟩-3,4-dihydroxybenzene]-2,2'-disulfonic acid (ammonium salt)	yellow	red-orange	
71	VIII	4-Hydroxy-3-carboxy-4'-nitroazobenzene-2'-sulfonic acid	light-yellow	bright orange	Limiting dilution 1:10^6
72	XX	2-Carboxy-benzene-⟨1-azo-1⟩-2-hydroxynaphthalene-3,6-disulfonic acid	orange	orange-red	
73	VIII, XVIII	4-Methoxybenzene-⟨1-azo-1⟩-1,8-dihydroxynaphthalene-3,6-disulfonic acid	rose	blue	
74	XX, VIII	2-Carboxybenzene-⟨1-azo-1⟩-1,8-dihydroxynaphthalene-3,6-disulfonic acid	rose	violet	In comparison with No. 80 the color develops ata higher pH
75	XIX	2-Carboxybenzene-⟨1-azo-1⟩-2-hydroxynaphthalene-4-sulfonic acid	dirty rose	violet	
76	XXIII	2,4-Dihydroxybenzene-⟨1-azo-1⟩-8 hydroxynapthalene-3,6-disulfonic acid	yellow-brown	dirty-rose	
77	XV,	8-Hydroxyquinoline-⟨5-azo-1⟩-benzene-4-sulfonic acid	orange	yellow	
78	III	4-Dimethylaminobenzene-4'-arsonic acid	orange	red-orange	
79	XXII	Benzene-2-arsonic acid-⟨1-azo-1⟩--2-hydroxynaphthalene 3,6-disulfonic acid	yellow	red-orange	
80	XXII, VIII	Benzene-2-arsonic acid-⟨1-azo-1⟩-1,8-dihydroxynaphthalene-3,6-disulfonic acid	rose	violet	Limiting dilution 1:3·10^6
81	XI	Rubeanic acid (in acetone)	light brownish	brownish	

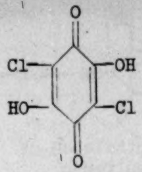
Formulas for the Reagents



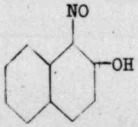
53. Sodium rhodizonate



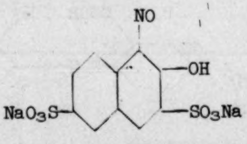
54. Picric acid



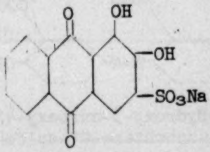
55. Chloranilic acid



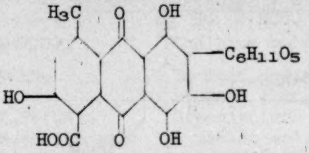
56. α-Nitroso-β-naphthol



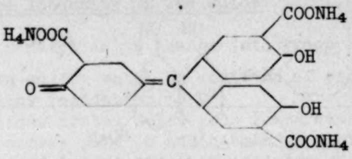
58. Nitroso-R-salt



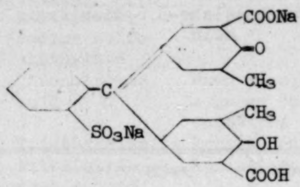
60. Alizarin-S



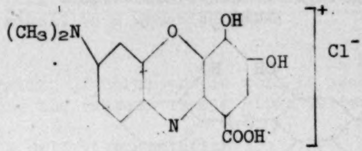
63. Carminic acid



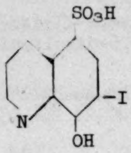
64. Aluminon



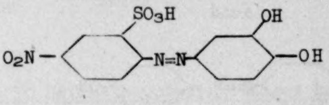
65. Eriochromecyanine-R



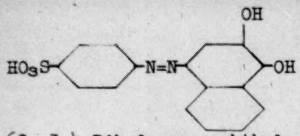
66. Gallocyanine,



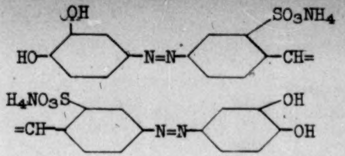
67. Ferron



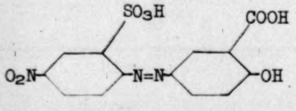
68. 3,4-Dihydroxy-4'-nitro-azobenzene-2'-sulfonic acid


OH
HO$_3$S
N=N
OH

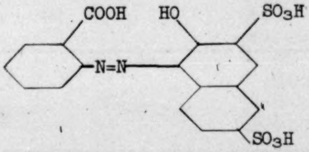
69. 3,4-Dihydroxy-naphthalene-⟨1-azo-1⟩-benzene-4'-sulfonic acid


OH
SO$_3$NH$_4$
HO
N=N
CH=
H$_4$NO$_3$S
OH
=CH
N=N
OH

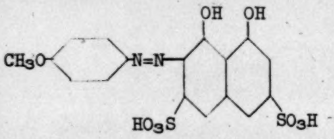
70. Stilbene-4,4'-bis[⟨-azo-1⟩-3,4-dihydroxybenzene]-2,2'-disulfonic acid


SO$_3$H
COOH
O$_2$N
N=N
OH

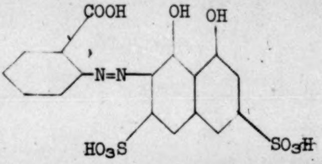
71. 4-Hydroxy-3-carboxy-4'-nitro-azobenzene-2'-sulfonic acid


COOH
HO
SO$_3$H
N=N
SO$_3$H

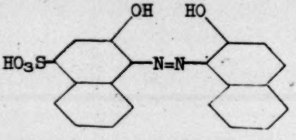
72. 2-Carboxybenzene-⟨1-azo-1⟩-2-hydroxynaphthalene-3,6-disulfonic acid


OH
OH
CH$_3$O
N=N
HO$_3$S
SO$_3$H

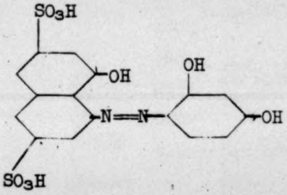
73. 4-Methoxybenzene-⟨1-azo-1⟩-1,8-dihydroxynaphthalene-3,6-disulfonic acid


COOH
OH
OH
N=N
HO$_3$S
SO$_3$H

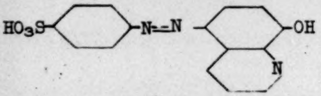
74. 2-Carboxybenzene-⟨1-azo-1⟩-1,8-dihydroxynaphthalene-3,6-disulfonic acid


OH
HO
HO$_3$S
N=N

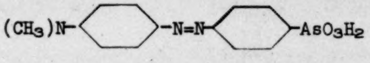
75. 2-Hydroxynaphthalene-⟨1-azo-1⟩ 2-hydroxynaphthalene-4-sulfonic acid


SO$_3$H
OH
OH
N=N
OH
SO$_3$H

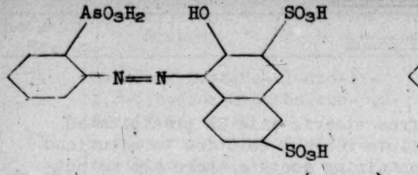
76. 2,4-Dihydroxybenzene-⟨1-azo-1⟩-hydroxynaphthalene-3,6-disulfonic acid



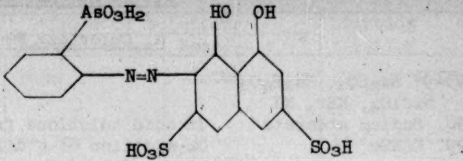
77. 8-Hydroxyquinoline-⟨5-azo-1⟩ benzene-4-sulfonic acid


(CH$_3$)N
N=N
AsO$_3$H$_2$

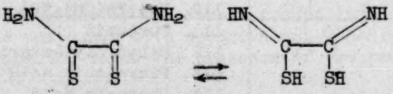
78. 4-Dimethylamino-azobenzene-4' arsonic acid



79. Benzene-2-arsonic acid-⟨1-azo-1⟩-2-hydroxynaphthalene-3,6-disulfonic acid



80. Benzene-2-arsonic acid-⟨1-azo-1⟩-1,8-dihydroxynaphthalene-3,6-disulfonic acid



81. Rubeanic acid

IV. Reagents Which Give Rise To A Change In The Color Of Vanadyl Salt Solutions Without Essentially Changing The Intensity Of The Color

82. NaH_2PO_4	The blue color of the vanadyl salts change into green
83. $KClO_3$	In acid media – a green color, which on addition of excess reagent changes to yellow (oxidation to V^5)
84. $K_4Fe(CN)_6$	Green colors for solutions cooled below room temperature
85. Rochelle salt	A violet color, which becomes pale on adding sodium acetate, and forms a greyish-red-violet solution on addition of ammonia
86. Sodium salicylate, sodium sulfosilicylate	In acid media, give a pale violet color, which changes on addition of NH_4OH or alkali to a greenish-brown
87. Chromotropic acid	When a colored preparation of chromotropic acid is used a green color develops; the reagent itself gives yellow solutions
37. Triethanolamine	Excess reagent gives a dull lilac solution
88. Nitrilotriacetic acid	An insignificant change in the characteristic blue color
89. o-Phenanthroline	Gives a green color in acid media, which subsequently turns yellow-brown; on addition of NH_4OH it becomes brown with formation of a precipitate
90. Thioglycollic acid	Greenish color

V. Masking Complexing Agents Which Do Not Lead To Definite Outward Changes But Which Prevent The Formation Of Precipitates After Addition Of Ammonia

91, 92, 85, 46 Glycerin, mannite, Rochelle salt, citric acid 86. Sodium Salicylate, sodium sulfosalicylate	Give rise to an appreciable change in the color to violet
88. Nitrilotriacetic acid	Causes an insignificant increase in the characteristic color of the $VOCl_2$

VI. Do Not Act Outwardly

a. Colorless Reagents

93-97 Na_2SO_3, $Na_2S_2O_3$
$NaClO_4$, KBr, KI
98. Sodium stearate — In acid solutions free stearic acid is precipitated
99. KCNSe — On addition of a dilute reagent solution to solutions of vanadyl salts containing acetate, there are no outward changes

100. Sodium dihydroxy tartrate
101. Ammonium maleate
102. Resorcinol
103. Urea
104. Dimethylglyoxime
105. α-Furildioxime
106. Diphenylcarbazide
107. 1,2-Aminonaphthol-4-sulfonic acid
108. Thiourea
109. Mercaptobenzothiazol (alcoholic solution)

b. Colored Reagents

110. $Na_2[Fe(CN)_5NO]$
111. Curcumin
112. Dihydroxytartaric osazone
113. Picrolonic acid
114. Picramic acid
115. Dithizone, shaken with a solution of dithizone in toluene

VII. The Most Sensitive Reactions For Quadrivalent Vanadium (adduced in Table 2)

TABLE 2

The reactions were carried out by the dropwise addition of a solution of urotropine or sodium acetate to an acidified solution of V^4 containing the reagent

Reagent No.	Reagent	Color of solutions		Limiting dilution
		Reagent alone	Reagent + V^4	
	Precipitation reactions			
14	8-Hydroxyquinoline	yellow	greenish brown precipitate	1:1,000,000
20	Sodium diethyldithiocarbamate	colorless	yellow-brown precipitate	1:2,000,000
16	Quinaldinic acid	colorless	light-yellow precipitate	1:330,000
7	Tannin	colorless	blue precipitate	1:1,000,000
	Color reactions			
40	Na_2CS_3	yellow	dark-brown	1:500,000
50	Pyrocatechol	colorless	dark-blue	1:2,000,000
48	Pyrogallol	colorless	dark-blue	1:2,000,000
49	Gallic acid	colorless	black-blue	1:2,000,000
64	Aluminon	almost colorless solution	turbid raspberry	1:10,000,000
65	Eriochromecyanine-R	rose	turbid violet	
58	Nitroso-R-salt	light-yellow	orange-yellow	1:250,000
71	4-Hydroxy-3-carboxy-4'-nitroazobenzene-2'-sulfonic acid	light-yellow	red-orange	1:500,000
80	Benzene-2-arsonic acid-⟨1-azo-1⟩-1,8-dihydroxynaphthalene-3,6-disulfonic acid (arsenazo) [12]	rose	violet	1:3,000,000

TABLE 2 (Contd.)

Reagent No.	Reagent	Color of solutions		Limiting dilution
		Reagent alone	Reagent + V^4	
74	2-Carboxybenzene-⟨1-azo-1⟩-1,8-dihydroxynaphthalene-3,6-disulfonic acid	rose	violet	1:2,000,000
61	4-Dihydroxyanthraquinone-2-sulfonic acid	yellow	lilac (changes rapidly)	1:10,000,000

VIII. Masking Complexing Agents For Quadrivalent Vanadium

Any reagent containing any of the atomic groups indicated previously, p.102, and which forms soluble compounds with quadrivalent vanadium, can be regarded as masking complexing agents, since the presence of the reagent can mask other reactions of V^4.

For practical purposes, reagents which contain groups V, XIV, and VIII are worthy of attention. Reagents with groups VI, IX and XXII also combine very firmly with V^4 and can yield soluble compounds; these compounds, however, are too intensely colored, and can therefore only be used for preventing the precipitation of V^4.

Nitrilotriacetates, oxalates, citrates and tartrates are good masking complexing agents; salicylates are much weaker.

An idea of the relative effectiveness of various masking complexing agents can be gained from the results given in Table 3.

TABLE 3

Masking Complexing Agents for Quadrivalent Vanadium

The concentrations of complexing agents given below practically fix completely 0.1 mg of vanadium^4 in 10 ml of a solution with regard to the action of reagent No. 80 (arsenazo [12])

Reagent No.	Masked reaction	Complexing agent	Amount of complexing agent which fixes 0.1 mg V^4 in 10 ml solution		
			mg/ml	mole/l	No. of moles of complex in agent fixing 1 atom V^4
46	$VOCl_2$+ Reagent No. 80 (0.2 mg V^4 in 10 ml)	Potassium nitrate	0.025	0.00011	0.67
85	Ditto	Rochelle salt	0.05	0.00018	0.90
88	Ditto	Nitrilotriacetate	0.037	0.00018	1.00
42	Ditto	Ammonium oxalate	0.03	0.00021	1.10
48	Ditto	Pyrogallol	0.03	0.00023	1.20
50	Ditto	Pyrocatechol	0.075	0.00068	3.40
86	Ditto	Sodium salicylate	0.3	0.0018	11.00

The values given in Table 3 were obtained as follows.

A standard was first prepared as follows. To ca. 9 ml of a solution containing 0.10 mg of V^4 and of pH = 6.0 (acetate buffer) was added that amount of reagent solution No. 80 so that the reagent was 50% saturated with respect to the quadrivalent vanadium, after which its volume was made up to 10 ml.

The amount of reagent is determined in a special preliminary experiment. Equal amounts of a solution of reagent No. 80 in a solution of the optimum pH for the development of the color of V^4 (pH = 6) were introduced into two identical test tubes. To one of these test tubes the V^4 solution was then added in small amounts until the violet color which developed did not change on addition of further V^4 solution. It is assumed that at this stage the given amount of reagent is 100% saturated with respect to vanadium. No vanadium was added to the other test tube containing the rose-colored reagent solution; consequently, the reagent is then only 0% saturated with respect to vanadium.

If the contents of both test tubes are observed together in a comparator after the volumes have been equalized, then the shade produced will correspond to the sum of the two, i.e., to a solution, the reagent in which is 50% saturated with respect to V^4 (Fig. 1). In order to determine the amount of vanadium necessary to give this 50% saturation of the reagent, the following procedure was adopted. The same amount of Reagent No. 80 solution as was used in the first test tubes together is introduced into a third test tube. Subsequently, when the necessary pH has been attained, a standard solution of V^4 is added to the third test tube until (after equalizing the volumes) the identical red-violet color is obtained as when the first two test tubes are examined simultaneously (i.e., the sum of the colors of test tubes 1 and 2). It is assumed that at this stage the amount of reagent present in the third test tube is sufficient to combine with 50% of the vanadium. On the basis of the amount of reagent No. 80 and of V^4 added to the third test tube, the amount of reagent which must be added to 0.1 mg of V^4 in order that 50% of the reagent is combined can be calculated.

A system in which the colored reagent is 50% combined with the given element is a very sensitive indicator for changes in the concentration of the free ions of this element in the solution. If, in our case, the amount of vanadium is somewhat less than that required, the red-violet shade will be redder, while for a higher vanadium content the shade will be bluer. A change in concentration of vanadium of 1-2% relative units is clearly shown by a change in shade.

The solution prepared in this way with a "50% color" can be used as a standard for experiments on the evaluation of the masking action of complexing agents.

In order to carry out these masking reactions the same amount of Reagent No. 80 as was used in the standard was introduced into a test tube and the solution adjusted to the requisite pH. 0.2 mg of vanadium was added however, and not 0.1 mg; the resultant color was violet. It was further established what amount of the test complexing agent was necessary to add to the given solution so that the color would match the color of the standard. Since only 0.1 mg of vanadium was used in the standard it was addumed that after attaining this stage the 0.1 mg of vanadium in excess would be combined with the complexing agent 1). For the concentrations of complexing agents used and under the experimental conditions employed, the colors formed by the complexing agents themselves, including pyrocatechol and pyrogallol, were so pale that there was no need to introduce any corrections for these colors 2).

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1) The use of such methods for the colorimetric determination of the instability constant of complexing compounds will be described elsewhere.

2) This fact indicates that the mechanism of masking is not so simple as would appear at a first glance.

In general, color reactions of V^4 with pyrogallol or pyrocatechol are adequately sensitive. The absence of colors when only low concentrations of these reagents are employed may be explained by the considerable dissociation of the compound formed, for the suppression of which it is necessary to increase the concentration of the reagents. But, on the other hand, from the observed facts on masking, it follows that V^4 forms compounds with these reagents even in very

(footnote continued on next page)

Nitrilotriacetates, citrates, tartrates, oxalates, and pyrogallol mask quadrivalent vanadium very fully. In the presence of these substances, V^4 is not precipitated by alkalis, quinaldinic acid, or other precipitants, and does not give color reactions.

Of course, the oxidation of quadrivalent vanadium to the quinquevalent state can also be regarded as masking which is very reliable.

IX. Oxidation-Reduction Reactions of Quadrivalent Vanadium

Under the effect of oxidizing agents with a suitable value of the oxidation potential, V^4 is oxidized to V^5. The graph showing the change in the oxidation reduction potential E_0 for the system V^5/V^4 with acidity, which is shown in Fig. 2, has been borrowed from the monograph on "Vanadometry" by V.S. Syrokomsky and Yu.B. Klimenko (Metallurgy Press, 1950, p. 6). Information is also given in this monograph on the behavior of V^4 toward oxidizing agents.

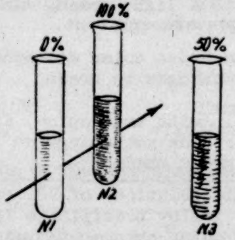

Fig. 1. Combined reagents for vanadium.

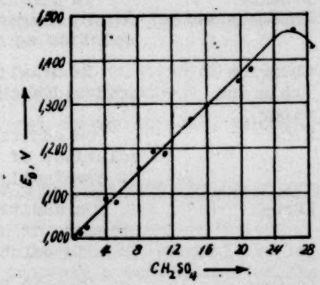

Fig. 2 The relation between normal potential and concentration (normality) of sulfuric acid.

The oxidized forms of oxidation-reduction indicators with values for the positive potential E_0 starting at approximately 1.06 and higher, can also act as oxidizing agents.

Color reactions of this type are given by the widely used oxidation-reduction indicator – phenylanthranilic acid. (the oxidized form is reddish-violet while the reduced form is colorless), and some other indicators – chiefly

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2) (Continued from page 114) dilute solutions.

A similar state of affairs has been observed in other cases. The color reactions of Fe^3 with the same reagent, viz. No. 80, is masked by low concentrations of salicylates, which themselves do not give observable colors with iron under the same experimental conditions.

We also observed that soluble colored complexes of barium are masked by very dilute solutions of sulfates which are not strong enough to cause the solution to become turbid as a result of $BaSO_4$[10].

It would be very tempting to postulate the formation of some intermediate compounds during masking; this however requires proof.

a number of derivatives of phenanthroline (Fe and Ru complexes) and of diphenylamine, information about which can be found in textbooks [5].

In alkaline media V^6, a strong reducing agent which is rapidly oxidized by aerial oxygen, reduces phosphomolybdic acid with the formation of a blue color (a sensitive spot test for vanadium), and reduces ferric salts, so that the ferrous salts formed can be detected by color reactions with dimethylglyoxime [8], or with o-phenanthroline [13], etc.

V^4 in acid media is reduced by strong reducing agents to V^3 and V^2. The formal potential of the system V^2/V^3 in sulfate solutions is equal to 0.36 V. V^4 is reduced to V^3 by bismuth amalgam [4, 14].

Reagents Which Oxidize V^4

116.	Aerial oxygen	In alkaline and ammoniacal solutions of V^4 the brown color gradually disappears.
39.	H_2O_2	In acid solutions a red colored solution is formed; if excess H_2O_2 is used the solution becomes yellow. This reaction gives the same result as the well-known reaction between quinquevalent vanadium and H_2O_2.
117.	Bromine (bromine water)	In alkaline solution (on addition of NaOH) the color changes from brown to a light green. In acid solution no outward changes are apparent.
118.	Chlorine (chlorine water)	In alkaline media the brown color disappears. In acid media the blue color changes to green.
119.	KIO_3	On addition to neutral (with urotropine) and acid solutions of V^4, the color does not change at first. It eventually acquires a green shade.
34.	$KBrO_3$	On addition to non-acid solutions of V^4, (in the presence of urotropine) a yellow precipitate is formed. In acid solution the blue color changes to yellow.
83.	$KClO_3$	In acid or neutral solution the blue color initially remains unchanged, but after standing for some time it changes to green.
120.	$NaNO_2$	In solutions of V^4 treated with urotropine, before the appearance of a weak turbidity which causes a change-over in the precipitate present from light brown to black, gas is evolved and the precipitate becomes a dirty green color. In weak acid solutions of V^4 a brown precipitate forms, which rapidly dissolves with the formation of a brown colored solution. Subsequently a light crystalline precipitate forms. Gas is evolved here also. In acid solutions a yellow-green precipitate is formed.
121.	$KMnO_4$	In neutral and acid solutions of V^4 the blue color changes to green. In alkaline media (NaOH) the solution is decolorized and a brown precipitate of manganese is formed.

Reagents Which Reduce V^4

122. Metallic zinc	In acid solution the color gradually changes from a blue through a green (V^3) into a violet (V^2) color.
123. $Na_2S_2O_4$	In a neutral urotropine solution of V^4, the blue color changes to a dark green. In an acid solution of V^4 there are no changes.

Oxidizing Agents and Reducing Agents Which Do Not React Outwardly With Quadrivalent Vanadium

116. Aerial oxygen	No appreciable changes occur in acid and neutral (with urotropine) solutionsof V^4 on standing for 2 hours in air. In acid solutions V^4 salts are completely stable to the air even when the solutions are heated [4].
124. Iodine	On the addition of iodine dissolved in alcohol or KI to acid or alkaline (NaOH) solution of V^4, no observable changes take place.
125. HNO_3	After acidification of aqueous solutions of V^4 with HNO_3 no oxidation occurs, even on heating.
126. $(NH_4)_2S_2O_8$	After a short heating period no changes initially occur in acid solutions of V^4.
127. $SnCl_2$	No changes occur in acid solutionsof V^4 or in solution neutralized with urotropine.
128. NH_2OH 129 NHH_4	There is no apparent change in acid, neutral, or alkaline solutions.

A Comparison Of The Reactions Of Quadrivalent Vanadium With The Reactions Of Other Elements

The analytical reactions of quadrivalent vanadium in general are reminiscent of those of quadrivalent titanium, which is probably a consequence of the adjacent positions occupied by these elements in the periodic system. They also resemble each other in their chromophoric action. Many reactions of quadrivalent titanium are characteristic of quadrivalent vanadium, and vice versa. For the V^4 reactions, however, the acidity must be less than for Ti^4 reactions. This is in agreement with the behavior of the two elements on hydrolysis; V^4 salts are not so easily hydrolyzed as those of Ti^4. By using sodium benzoate or ammonium cinnamate it is possible to separate V^4 from bivalent and other cations which hydrolyze with greater difficulty than V^4 [7].

With regard to the action of organic colored reagents with oxygen-containing groups, the reactions of V^4 also resemble those of aluminum, the color reactions of which have been considered before [6]. Both these elements form similar colors under similar conditions. The behavior of V^4 to sulfur-containing reagents is reminiscent of the behavior of Mo^6 to these reagents.

Quadrivalent vanadium resembles aluminum and titanium in its behavior toward reagents containing amine nitrogen, while it differs considerably from those elements for which combination with amine nitrogen is very characteristic (copper, nickel, cobalt).

Salts of quadrivalent vanadium in acid solution do not oxidize appreciably in the air; in alkaline solution, however, oxidation is very rapid. Salts of V^4 in acid solution are more stable to air than ferrous salts; in alkali the reverse is true.

SUMMARY

A list is made in this article of atomic groups, the presence of which in the molecules of organic reagents determines the capacity of these reagents to interact with quadrivalent vanadium. The behavior of V^4 toward 129 inorganic and organic reagents, which are divided into groups according to the analytical effect of their reactions (precipitation, color reactions, masking complexing agents), is considered. A list is given of the most sensitive reactions for V^4, and the elements whose analytical reactions resemble those of quadrivalent vanadium are indicated.

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2) See Consultants Bureau English Translation, page 255 ff.

THE DETERMINATION OF TUNGSTEN IN MULTI-COMPONENT ALLOYS

R.B.Golubtsova

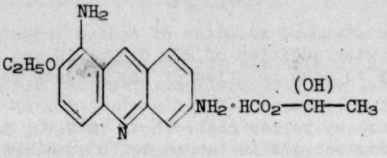
The widely used method of determining tungsten in steel by acid hydrolysis is not very satisfactory for the analysis of multi-component alloys containing appreciable amounts of titanium, zirconium, vanadium, chromium and other elements. In the presence of the elements indicated, the precipitate of tungsten trioxide is always contaminated with the oxides of these metals, so that corrections must be applied, and the acid hydrolysis method accordingly becomes rather lengthy.

Application of the acid hydrolysis method to the determination of tungsten in multi-component cast iron has the following disadvantages: the graphite which separates at the same time as the tungstic acid does not burn completely at the temperature allowed for calcining the precipitate of tungsten trioxide; a higher temperature leads to loss of tungsten through sublimation. For the purification of tungstic acid from contaminants, we successfully applied the method of dissolving the precipitate in ammonia and subsequently precipitating it (on acidification of the solution with HCl), with such organic precipitants as β-napthoquinoline [1, 2]; 6-toluquinaldine [3], and pyramidone [4]. Of these reagents, β-naphthoquinoline is widely used in practice.

The aim of the present work was a search for a new, easily synthesized and easily available precipitant for tungsten which could be used as a routine method for the determination of tungsten in multi-component alloys.

All the precipitants suggested for tungsten are organic compounds containing nitrogen. In our search for a new reagent we tested a number of such compounds. As a new reagent which was first applied [5], we tried the lactate of 2-ethoxy-6,9-diaminoacridine, which is the lactate of the acridine derivative known as "Rivanol". "Rivanol" is widely used in medicine as an antiseptic for various infections; it is a fine crystalline powder with a bitter taste; one part by weight of it dissolves in 50 parts of cold water, 9 parts of hot water, or 10 parts alcohol. It is insoluble in ether.

The formula of "Rivanol" is as follows $C_{18}H_{20}O_4N_3$:



Molecular weight 343.19.

From the formula it is clear that "Rivanol" is an amino compound.

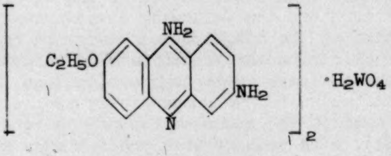
For a preliminary test of the reagent as a precipitant for tungstic acid a 2% solution of "Rivanol" was prepared (2 g dissolved in 100 g with slight heating).

In order to establish the composition of the compound, a standard solution of sodium tungstate was made acid to litmus with HCl (sp.gr. 1.19) and 3 drops in excess added. 20 ml of the 2% "Rivanol" solution was then added. The coagulated precipitate was filtered through a No. 4 sintered glass filter and washed 3 times with 2% "Rivanol" solution. The precipitate obtained was dried in a desiccator, after which it was transferred to an oven and dried at 100°.

Preliminary analysis of the precipitate obtained suggests that one atom of vanadium is equivalent to 2 molecules of "Rivanol".

Calculated from the formula	Found experimentally
W = 24.4%	W = 25.0%
C = 40.7%	C = 40.5%
N = 10.1%	N = 10.61%

On the basis of the results obtained the composition of the compound should correspond to $(C_{15}H_{15}ON_3)_2 \cdot H_2WO_4$.



(rivanol tungstate).

In order to determine the specificity of "Rivanol" as a precipitant for tungstic acid, qualitative tests were carried out on the salts of various metals, in which 5 ml of 2% (aqueous) "Rivanol" was added to solutions of the various salts in aqueous sulfuric and hydrochloric, respectively. Qualitative tests were made on the salts of tungsten, bivalent and trivalent iron, and salts of cobalt, nickel, zinc, cerium, beryllium, titanium, vanadium, niobium, chromium, manganese and molybdenum. It was observed that "Rivanol" only precipitates the tungsten ion in HCl at a pH of 3-4. In weak HCl, molybdate is also precipitated.

The Method of Determining Tungsten In Solutions of Its Pure Salts

In Sulfuric Acid Solutions To the standard solution of sodium tungstate made acid to methyl orange with H_2SO_4, sp.gr. 1.84, 5-10 ml of 2% aqueous reagent solution is added.

In Hydrochloric Acid Solutions The standard solution of sodium tungstate is made acid to methyl orange by the dropwise addition of HCl, sp.gr. 1.19, and 3 drops added in excess. 5-10 ml of the 2% aqueous solution of the reagent is then added.

The precipitate formed, which has a creamy yellow color (both in H_2SO_4 and HCl solution), easily coagulates after a few seconds in the cold. To accelerate coagulation, the solution may be heated on a water bath. (Solution and precipitate can be left overnight).

The precipitate is filtered through a fine filter (blue ribbon) covered with a fine layer of ashless paper pulp, and then washed 3-4 times with dilute HCl (1 ml HCl, sp.gr. 1.19, in 400 ml water). The washed precipitate is then dried and ignited in a porcelain crucible in a muffle, first at a low temperature, and then at 600°. The weight obtained is multiplied by a factor of 0.7931.

Results for the determination of tungsten in solutions of its pure salts determined by this method are given in Table 1.

TABLE 1

No.	W taken, in % (as NA_2WO_4)	W found, in %	Amount of reagent added, in ml.
1	0.33	0.35; 0.36	1
2	0.48	0.49; 0.50	
3	0.73	0.74; 0.76	2
4	0.98	1.02; 1.03	
5	1.11	1.09; 1.06	
6	1.82	1.80; 1.86	3
7	2.05	2.06; 2.07	
8	2.44	2.47; 2.42	6
9	2.63	2.63; 2.58	
10	2.96	2.93; 2.99	
11	3.59	3.65; 3.62	
12	4.88	4.87; 4.82	10
13	5.55	5.50; 5.49	
14	6.12	6.03; 6.06	

The results obtained were satisfactory, as can be seen from Table 1. The method was therefore tried out on standard steels and also on multi-component alloys, including multi-component cast iron. In these alloys the tungstic acid was separated after dissolving in acid by the acid hydrolysis method, and then reprecipitated from ammoniacal solution.

The results obtained are given in Tables 2, 3, and 4.

TABLE 2

Determination of Tungsten in Standard Steels

No. of Steel	W, %	W found, %
104	0.96	0.97; 1.02
105	2.74	2.76; 2.80
111	2.48	2.48; 2.42
122	8.78	8.80; 8.80

TABLE 3

Determination of Tungsten in Cast Iron

No.	W, %	W found, %
1	2.21	2.24
2	2.67	2.65
3	3.11	3.14
4	4.39	4.40
5	5.60	5.65

As already shown [5], in the case of multi-component alloys which contain niobium and tungsten simultaneously, the latter can be precipitated by various organic precipitants after its separation from niobium. In this case the tungsten is found in the filtrate after the separation of tungsten and niobium with a mixture of manganese sulfate, ammonium chloride and ammonia. The filtrate is made acid to methyl orange by dropwise addition of HCl, sp.gr. 1.19, and a few drops added in excess, after which the solution is boiled in order to destroy carbonates. The tungsten is then precipitated with "Rivanol".

We carried out determinations of tungsten in alloys containing niobium. The results obtained were satisfactory. (Table 6).

TABLE 4

Determination of Tungsten in Alloys in the Presence of Titanium1)

No.	W,% found colorimetrically by Feryanchich's method [6]	W,% found by precipitation with β-naphthoquinoline	W,% found by the "Rivanol" method	% of Ti in the alloy
1	1.16	1.18	1.16	2.97
2	2.16	2.20	2.14	3.12
3	4.20	4.07	4.11	3.60
4	4.89	5.04	5.01	3.76
5	5.42	5.53	5.57	5.23
6	6.00	6.10	6.14	6.08

TABLE 5

Determination of Tungsten in Alloys in the Presence of Zirconium

No.	W,% found colorimetrically by Feryanchich's method [6]	W,% found by precipitation with β-naphthoquinoline	W,% found by the "Rivanol" method	% of Zr in the alloy
1	3.02	3.12	3.08	0.50
2	4.22	4.08	4.12	1.96
3	4.25	4.16	4.20	2.92
4	5.00	5.09	5.14	4.10
5	6.30	6.18	6.12	6.44

TABLE 6

Determination of Tungsten in Multi-component Alloys Containing Niobium

No.	W found, in %	
	By precipitation with β-naphthoquinoline	By precipitation with "Rivanol"
1	2.51	2.50; 2.54
2	4.44	4.46; 4.48
3	5.30	5.36; 5.38
4	6.22	6.27; 6.27
5	7.14	7.09; 7.10
6	8.73	8.70; 8.67
7	9.53	9.58; 9.64
8	10.12	10.08; 10.20

Analytical Procedure

Alloys based on iron, cobalt, and chromium and cast iron are dissolved in 80 ml HCl (1:1) with strong heating. When the alloy is completely dissolved, 5 ml of HNO_3, sp.gr. 1.40 is added to oxidize it. Alloys on a nickel basis are dissolved in a mixture of 60 ml HCl (1:1), and 5 ml HNO_3, sp.gr. 1.40. When the sample has dissolved, (the weight taken will depend on the amount of tungsten in the alloy) the solution is evaporated to a paste like consistency

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1) When 3-6% of titanium is present, the weight of alloy taken for analysis is decreased to 0.5 g in order to decrease the adsorption of titanium by the precipitate of tungstic acid. In the presence of up to 3% titanium the precipitate of tungsten does not entrap more than 0.3% titanium, which does not affect the subsequent steps in this analytical method, and does not affect the completeness of the extraction of tungstic acid by ammonia.

and carefully dried by heating on a thin layer of asbestos on a hot plate. 50-60 ml HCl (1:4) is added to the dry residue and the whole heated in a beaker fitted with a cover glass for 1 hour at a moderate temperature. 100 ml of hot distilled water is then added to the solution and the whole heated again for another hour. The precipitate of tungstic acid which is formed is filtered off on a fine filter covered with a thin layer of ashless paper pulp and washed with 10% HCl until no reaction for iron is given (test the filtrate with a crystal of potassium ferrocyanide or ammonium thiocyanate on a white porcelain plate).

The washed precipitate and filter are transferred into the same beaker from which the precipitate was originally filtered, and the paper filter disintegrated thoroughly. 50 ml of hot ammonia water is added (1 part ammonia and 1 part hot water), and the whole heated for 30 minutes on a boiling water bath. The liquid is filtered and the precipitate washed by decantation, after which it is transferred to an ashless filter paper and washed with a 10% solution (by volume) of hot ammonia. During this procedure the tungstic acid dissolves completely.

The ammoniacal filtrate is acidified (to methyl orange) with HCl, sp.gr. 1.19, and 3-4 drops added in excess. The tungstic acid is precipitated by addition of 5 ml of 2% "Rivanol" for each 2.5% W (for a sample weight of 1 g). The precipitate is coagulated by standing in the cold or on a water bath; the solution can be left overnight. The precipitate is filtered off, and washed 2-3 times with dilute HCl (1 ml HCl, sp. gr. 119, in 400 ml of water).

The washed precipitate is transferred to a weighed porcelain crucible, dried, and then calcined, first at a low temperature in order to avoid sublimation of the tungsten, and then at a temperature not higher than 600-650° in a muffle. The conversion factor is 0.7931 for tungsten.

SUMMARY

1. A new, available reagent - "Rivanol" - is suggested for the quantitative determination of tungsten in multi-component alloys (based on iron, nickel, cobalt, and chromium) and cast iron.

2. By means of this method tungsten can be determined in the presence of large amounts of titanium, zirconium, vanadium, chromium, nickel, cobalt, and other alloy components.

3. The method is being used in factory laboratories.

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"NON-DESTRUCTIVE SPOT TESTS" FOR IRON IN COPPER ALLOYS USING DIMETHYLGLYOXIME IN ACID SOLUTION

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A large number of organic reagents have been proposed in recent years for the colorimetric determination of small amounts of iron. These include α-α'-dipyridyl, thioglycollic acid, nitroso-R-salt etc.. Because of the limited distribution of these reagents in factory practice, ammonium thiocyanate is the reagent most frequently used.

The thiocyanate reaction is one of the most sensitive reactions, and has been in use for a long time. Nevertheless it is not completely suitable for the colorimetric determination of iron.

As Babko [1], has shown the color is caused by the complex ion $FeSCN^{2+}$, the instability constant of which is $5 \cdot 10^{-3}$. The fact that this constant has such a high value also determines the large change in intensity of the color with temperature, thiocyanate concentration, and the presence of other anions.

Daniel and Garner [2], found that the color of the iron-thiocyanate complex is not stable even in isoamyl alcohol, and that its intensity is strongly dependent on the nature of the acid and the temperature.

Ovenston and Parker [3], showed that the color is only stable (for 20-25 minutes) when it has been obtained under strictly controlled acid and thiocynate concentrations, and by the use of high grade thiocyanate.

For the determination of iron in copper alloys by the "non-destructive spot test"[1] method, therefore, we tried to use the very sensitive reaction of iron with dimethylglyoxime in ammoniacal solutions proposed in 1914 by the Russian scientists Chugaev and Orelkin [4]. Their colorimetric method consists essentially in reducing trivalent iron to the bivalent state with hydrazine sulfate in acid solution and then adding an alcoholic solution of dimethylglyoxime in ammonia until the smell of ammonia persists.

Griffing and Mellon [5], with the same end in view, reduced the trivalent iron to the bivalent state, and then stabilized the color by means of an ammoniacal solution of sodium hydrosulfite ($Na_2S_2O_4$). Initially we tried to reduce Fe^{3+} to Fe^{2+} by means of stannous chloride with subsequent addition of sodium hydroxide to get the required alkaline conditions. It was found, however, that in order to dissolve the precipitates of $Sn(OH)_2$ and $Sn(OH)_4$ formed, a large excess of alkali was necessary, and the color thus developed had a shade which was completely unsuitable for colorimetric determination.

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[1] Without taking borings, scrapings, or clippings from the metal to be tested.

We observed that when dimethylglyoxime and an excess of sodium hydroxide were added to the solution of iron reduced by stannous chloride, a color developed which did not disappear on subsequent acidification. When ammonia was used instead of NaOH to get the requisite alkaline conditions, the color developed was unstable in acid solution and disappeared even at a pH of 6. We did not find any mention of this phenomenon in the literature.

We therefore made a more detailed study of the conditions of formation of the colored compound and of its stability, and also of the sensitivity of the reaction and its possibilities as a basis for colorimetric method for iron.

Conditions For The Formation Of The Color If to a solution of bivalent iron reduced by stannous chloride is added a 1% solution of dimethylglyoxime in 5% NaOH, and the solution adjusted so that its pH is > 4.8, a dirty red color develops which, on addition of acid to lower the pH to 2 or lower, does not disappear, but changes into a red or rose (if the amount of iron is very small) color.

When sulfurous acid or hydrazine sulfate were used as reducing agents the results were unsatisfactory, because of the development of a color which proved unstable in acid solution. Moreover, the color obtained was stable only when NaOH and not NH_3 was used for getting the requisite pH.

These facts give a basis for assuming that stannous chloride and NaOH have a positive effect on the formation and stabilization of the colored complex of dimethylglyoxime with bivalent iron in acid solutions.

In order to check on the stability of the color we carried out two series of experiments. The original solution contained $5 \cdot 10^{-5}$ g of iron/ml, 1 ml of this solution was measured into a measuring cylinder and 3-4 drops of 10% stannous chloride added. After 1 minute, 10 drops of an alkaline solution of dimethylglyoxime and 5 drops of NaOH were added. The solution was mixed and concentrated HCl added until the precipitate dissolved. When the solution had been diluted to 10 ml it was left to stand in the light.

Further 1 ml lots of the original solution were then taken at various time intervals and treated as described above, and the intensities of the colors compared visually with the color of the first solution. When this was done no difference in intensity was observed between the color of the solution prepared first and those of solutions prepared after various time intervals.

In the second series of experiments, the color intensity was measured with a photocolorimeter of the UNIKhIM type (without light filters). For this purpose colored solutions of various concentrations were prepared. Using a cell with a 10 mm layer thickness, the value of the light absorption for these colored solutions was measured after 15 minutes, 1 hour, etc., from the time of development. The results obtained are given in Table 1.

From these results it is clear that the stability of the color of the iron-dimethylglyoxime complex in acid solution is very high.

It was found experimentally that the sensitivity of the given reaction equals $5 \cdot 10^{-4}$ g of metallic iron/ml, i.e., it is equal in sensitivity to the thiocyanate reaction (without extraction).

It was also shown that the colors of the reaction obey Beer's law closely for iron concentrations of $5 \cdot 10^{-4}$ g/ml or less.

Manganese, cobalt, cadmium, zinc, lead, aluminum, and the alkaline earth elements in amounts of not more than 100 times that of iron do not interfere with the reaction. Neither do copper, bismuth, chromium and nickel, in amounts not exceeding that of iron by 20 times, interfere. In large amounts they do interfere, particularly copper.

For the determination of iron in copper alloys, therefore, where the amount of iron is 100-200 times less than that of the copper, it is essential to remove the copper first. Other elements which occur in the copper alloys do not interfere.

TABLE 1

No.	Concentration of iron in solution g/ml	Photocolorimeter scale readings after;							
		15 min.	50 min.	2 hours	22 hours	45 hours	50 hours	3 days 5 hours	8 days 5 hours
1	$1.6 \cdot 10^{-6}$	15.3	15.2	15.0	15.3	15.5	15.3	15.5	15.3
		14.9	15.0	14.6	15.2	15.3	14.5	15.0	
2	$3.5 \cdot 10^{-6}$	19.9	19.6	20.5	20.8	20.7	19.9	20.1	20.6
		20.0	19.8	19.6	20.0	20.5	19.3		
3	$5.1 \cdot 10^{-6}$	38.3	37.9	38.0	38.5	37.9	37.2	36.5	36.8
		38.0		38.0	37.5		37.9		
4	$7.5 \cdot 10^{-6}$	52.0	52.0	52.2	52.8	52.3	51.5	51.0	51.5
		51.3			51.5		52.8		

Colorimetric Determination of Iron By The "Non-destructive Spot Test Method"

Two or more drops (according to the expected amount of iron in the alloy) of nitric acid (1:1) are placed on the cleaned alloys surface. When the reaction has finished the solution is transferred to a test tube and the surface of the sample is washed 2-3 times with 2-3 drops of water. A drop of sulfuric acid (1:3) is then added and the solution heated to the boil. 0.05 g of cadmium sulfide is added to the hot solution to remove the copper. The precipitate sulfides are filtered on a 3-4 cm diameter filter and washed 2-3 times with hot water. The filtrate is diluted with water to 10 ml and mixed. 1-3 ml of the solution is transferred with a pipet to another cylinder, and having added two drops of concentrated HCl, 3 drops of stannous chloride solution and 3 drops of 20% Rochelle salt are added and the whole heated to the boil (to reduce the iron).

10 drops of the solution of dimethylglyoxime and 5 drops of 20% NaOH are then added, and when the solution has been mixed, concentrated HCl is added dropwise (5-7 drops) until the precipitate has dissolved. Both standard and test samples are treated thus (The same standard can be used for several drops).

The intensity of the red color obtained is determined colorimetrically. Water is used for dilution when matching the intensities of the colors of the test and standard solutions. The amount of iron is determined from the formula $C_{T.S.} = \frac{V_{I.S.}}{V_{S.S.}}$ where $C_{T.S.}$ and $C_{S.S.}$ are the percentages of iron in the test and standard samples respectively; $V_{I.S.}$ and $V_{S.S.}$ are the volumes of the test and standard solution when the colors are matched.

The time for one determination, including dissolving the sample, is 15-20 minutes; for a series of determinations 10-15 minutes. Some of the results obtained by this method are adduced in Table 2. S.O No. 89, with an iron content of 0.20%, was used as the standard.

In conclusion I wish to thank Prof. I.A.Tananaev for his advice.

SUMMARY

1. It has been established that the colored complex formed between di-

TABLE 2

No.	Designation of test sample	Fe found %		Deviation
		By the method described	Volumetric method	
1	No. 15	0.14	0.13	+0.01
2	(OTsS Bronze)	0.11_3	0.13	−0.017
3		0.14		+0.01
4		0.12_4		−0.006
5		0.14_6		+0.014
6		0.15		+0.02
	Average..............	0.13_5	0.13	+0.005
1	S.O. No. 66	0.17		0.000
2	(Muntz brass)	0.15		−0.020
3		0.18	0.17 (by rating)	±0.010
4		0.14_5		−0.025
5		0.19		+0.020
6		0.18		+0.010
	Average...............	0.17	0.17	0.000
1	No. 16	0.23	0.22	+0.01
2	(OTsS Bronze)	0.22		+0.00
3		0.24		+0.02
4		0.23		+0.01
5		0.21		−0.01
	Average..............	0.22_6	0.22	+0.006
1	S.O. No. 68	2.52	2.62	−0.10
2.	(AZhM Bronze)	2.69	(by rating)	+0.07
3		2.56		−0.06
4		2.76		+0.14
5		2.63		+0.01
6		2.75		+0.13
	Average..............	2.65	2.62	+0.13

methylglyoxime and bivalent iron is very stable in acid solutions.

2. It has been shown that the sensitivity of the iron-dimethylglyoxime reaction in acid solutions is $5 \cdot 10^{-7}$ g iron per ml.

3. It has been shown that the reaction of bivalent iron with dimethylglyoxime in acid solution can be used for the colorimetric determination of small amounts of iron in copper alloys.

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FURYLDIOXIME AS A REAGENT FOR THE GRAVIMETRIC AND COLORIMETRIC DETERMINATION OF NICKEL

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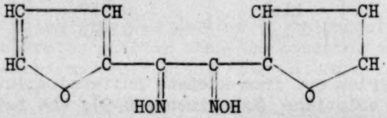
L.A.Chugaev in his classic work "Investigations in the Field of Complex Compounds" [1], describes the properties of a number of compounds formed between α-dioximes and metals chiefly of the eighth group of the Mendeleev Periodic Table. From a systematic investigation of this class of compounds it is clear that many of the compounds belonging to this class are of analytical interest. It is known that the molecular structure of the dioxime affects the properties of the nickel compound of the given dioxime [2]. The testing of a new reagent is, therefore, of both practical and theoretical interest.

Gravimetric Determination of Nickel



Chugaev was first to isolate the nickel derivative of α-furyldioxime and establish its composition; he found 11.85% of nickel (the theoretical value is 11.81%; it was determined as the oxide. There is some information in Soule's article [3], on the analytical application of this reagent. The compound at our disposal had a m.p. of 168.3° and at 19-20° 0.22 g of the α-furyldioxime dissolved in 100 g of water, while at 85-90° the solubility was 2 g/100 ml. We used a 0.2% aqueous solution for gravimetric determinations and a 1% alcoholic solution for colorimetric determinations. All weighings were on a micro scale. The nickel solution used was standardized gravimetrically, the nickel being precipitated as the dimethylglyoxime compound [2]. The standard solution contained 1.172 mg/ml. Preliminary experiments indicated that the pH is of great importance in ensuring complete precipitation of the α-furyldioxime. The nickel solutions were weighed out. The experiments were carried out as follows. Various amounts of ammonia, and α-furyldioxime in 100% excess, were added to the nickel solution heated to 60-80°. The solution became red immediately and, on standing for 10-15 minutes with stirring, a flocculent, well-coagulated precipitate of a dark red color formed. In some of the experiments the precipitate had a brick-red color, but this did not affect the results. The precipitate, which was filtered off on a porcelain microcrucible, was washed with a saturated solution of nickel α-furyldioxime, and once or twice with cold water.

From Table 1 it is clear that the precipitation of small amounts must be carried out from 25 ml.

It was also determined at what pH the nickel α-furyldioxime is precipitated quantitatively. The results are given in Table 2

TABLE 1

No.	Volume, in ml	Ni taken, in mg	pH	Ni found, in mg	Absolute error, in mg
1	50	0.586	8.95	0.528	-0.058
2	50	0.586	9.61	0.538	-0.048
3	25	0.494	9.61	0.483	-0.011
4	25	0.524	9.61	0.523	-0.001
5	25	0.512	9.61	0.514	+0.002

TABLE 2

No.	Ni taken, in mg	pH	Ni found, in mg	Absolute error, in mg
1	1.17	2.1	no ppt.	
2	1.17	3.4	no ppt.	
3	1.1	4.0	0.12	-0.98
4	0.494	4.9	0.232	-0.262
5	0.494	6.17	0.467	-0.027
6	0.498	6.4	0.489	-0.011
7	0.494	6.6	0.487	-0.007
8	0.502	8.0	0.504	+0.002
9	0.505	10.5	0.508	+0.003
10	0.498	10.5	0.497	-0.001
11	0.498	11.1	0.417	-0.081
12	0.505	11.5	0.421	-0.084

Precipitation was carried out from acetate buffered solutions (Experiments 1-5), and from ammoniacal solutions (Experiments 6-9); the total volume in all cases was 20-25 ml.

From Table 2, it is obvious that precipitation is complete in the pH range 6.4-10.5. In practice, it is convenient to carry out the precipitation in the presence of an indicator. We used neutral red and phenolphthalein as indicators, ammonia being added till the color changed, before addition of the reagent. Nickel was also determined by the α-furyldioxime method in the presence of other elements.

Determination of Nickel in the Presence of Iron and Aluminum

Analytical grades of ferric chloride and aluminum chloride were used. The determinations were carried out in the presence of Rochelle salt, 10 ml of a 10% solution being added for a nickel to iron and aluminum ratio of 1:10; and 20 ml when the ratio of nickel to iron and aluminum was increased to 1:100, for a total volume of 100 ml. The results obtained are adduced in Table 3.

From Table 3 it is clear that nickel is precipitated quantitatively (under the conditions indicated). All the results cited for the gravimetric determinations of nickel are the means of replicate experiments.

The Colorimetric Determination Of Nickel

Chugaev [1], who studied the capacity of the metal derivatives of α-dioximes to dissolve in organic solvents, considered this property to be an indication that they belong to the class of intramolecular compounds. In our work we tested the solubility of nickel α-furyldioxime in organic solvents to form colored solutions suitable for colorimetric determinations. A Pulfrich photometer was used, and the nickel sulfate used was analytical grade; the solutions were calibrated as indicated above. The completeness of extraction with the organic solvent depends to a very large extent on the pH of the aqueous solution. We studied the extraction of nickel α-furyldioxime from buffered solutions with pH's from 5.6-9.1 with chloroform and benzene, and found that extraction was quantitative within the pH limits of 7.3-8.4. The following conditions were observed for the determination of nickel in solutions of its pure salt.

TABLE 3

No.	Ni taken, in mg	Ratio of Ni:Fe	Ni found, in mg
1	3.3	1:10	3.2
2	3.3	1:100	3.3
		Ni:Al	
3	1.1	1:10	1.07
4	1.1	1:100	1.2

To 20-25 ml of the aqueous nickel solution contained in a separating funnel was added 1-2 ml of 10% sodium acetate solution, and then dropwise a 10% solution of ammonia or 1 N alkali until the solution was alkaline to litmus, when 2-3 drops were added in excess. To the solution were added 10 ml of chloroform or benzene and a 1% alcoholic solution of α-furyldioxime in 50-100% excess. After gentle shaking for 2-3 minutes the layer of organic solvent was removed, and the aqueous solution was extracted with two more lots of solvent (5 ml each). In order to remove traces of water in the chloroform or benzene layers, the solution was filtered through a dry filter paper or poured into a dry flask where the water is held on the sides of the flask.

We found that the solubility was greater in chloroform, and also that the chloroform layer separates quicker than the benzene, so that in all our subsequent work we used chloroform. Using this method, a light absorption curve was taken (Table 4 and Fig. 1).

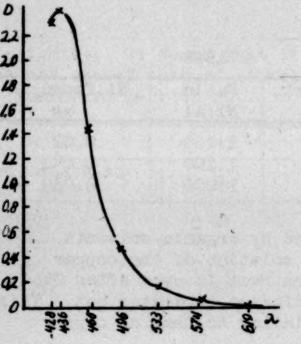


Fig. 1 Light absorption curve for nickel furyldioxime. Concentration $1.2 \cdot 10^{-4}$ M.

Chloroform was used as the blank solution; the nickel concentration was $1.2 \cdot 10^{-4}$ M, and the cell used was a 2 cm one (Table 4).

Maximum light absorption occurs in the visible spectrum at a wave length of 432 mμ; a violet light filter was used. Using this light filter, a calibration curve was drawn for nickel for a concentration range of 0.005 to 0.2 mg, using a 1 cm cell (Table 5 and Fig. 2).

The colored solutions obey Beer's law (from 0.0175 mg Ni) and the reaction is characterized by high sensitivity; for a 1 cm cell, 0.005 mg nickel has a D of 0.088, which indicates the color intensity of the solution. When a 2 cm cell is used, considerably smaller amounts of nickel can be determined.

Determination of Nickel In The Presence of Iron Aluminum and Magnesium

For the determination of nickel

in the presence of aluminum and iron [3], 3-4 ml of a 10% solution of sodium tartrate or Rochelle salt was added to 20 ml of the test solution. The other experimental conditions were identical to those used for the determination of nickel in its pure solutions.

TABLE 4

Wave length, in mμ	D	E	Wave length, in mμ	D	E
426	2.3	9581	533	0.175	725
432	2.4	10000	574	0.075	283
465	1.45	0041	619	0.025	104
496	0.52	2161	665	0.015	62

TABLE 5

Ni, in mg	D
0.005	0.088
0.0088	0.328
0.0175	0.590
0.111	1.625
9.175	2.60
0.20	2.97

The calibration curve was constructed by using solutions of pure nickel salt.

Measurements were made on a MOSKIP photocolorimeter. The results are given in Tables 6 and 7.

It was also established that the presence of magnesium did not interfere with the determination of nickel under the conditions used for the determination of nickel in its pure salt solutions, as can be seen from Table 8.

We were also interested in studying the behavior of the dioximes of other metals toward organic solvents, in particular those of copper and cobalt, which often accompany nickel in its natural state. It was found that cobalt α-furyldioxime is extracted by benzene and chloroform; maximum light absorption occurs in the ultraviolet. The results are not reproducible because of the difference in degrees of oxidation of the cobalt; cobalt was extracted as the bivalent cobalt dioxime. It was not found possible to find conditions suitable for the determination of nickel with α-furyldioxime in the presence of cobalt.

TABLE 6

Ni taken, in mg	Ratio Ni:Fe	Ni found, in mg
0.058	1:100	0.058
0.116	1:100	0.115
0.58	1:100	0.58

TABLE 7

Ni taken, in mg	Ratio Ni:Al	Ni found, in mg
0.02	1:100	0.02
0.04	1:100	0.041
0.04	1:200	0.039

Copper α-furyldioxime is quantitatively extracted by organic solvents, though extraction is rather slow (6-7 minutes). The solution of the copper dioxime in chloroform is unstable; benzene does not extract it even after 24 hours. On standing for a longer time, copper α-furyldioxime separates out. This oxime has a greyish black color, with a composition similar to that of copper dimethylglyoxime [2].

The absorption spectra for copper α-furyldioxime is given in Table 9, and Fig 3, for a concentration of $5 \cdot 10^{-5}$ M for copper and using a 2 cm cell.

Maximum light absorption occurs in the visible at a wave length of 465 mμ, i.e., somewhat higher than for nickel. Nickel cannot therefore be determined in the presence of copper without first removing the latter. Alexander and Goder [4] suggest a method for the separation of small amounts of nickel

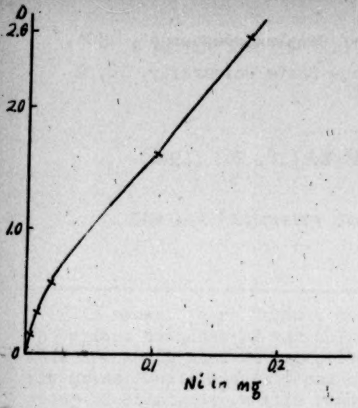


Fig. 2 Relation between optical density and nickel concentration.

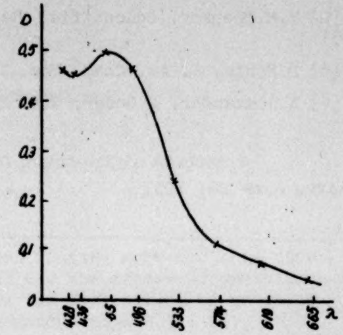


Fig. 3 Light absorption curve for copper α-furyldioxime. Concentration $5 \cdot 10^{-5}$ M.

TABLE 8

Ni taken, in mg	Ratio of Ni:Mg	Ni found, in mg
0.02	1:10	0.02
0.04	1:100	0.04

and copper, by first extracting the dioximes with chloroform and then washing out the copper dioxime with ammonia, while the nickel dioxime is broken down with hydrochloric acid and then determined colorimetrically.

In conjunction with Babicheva we checked this method, and also modified it slightly. We found that it can only be employed when the copper concentration does not exceed that of nickel. Further detailed examination of the method was not therefore carried out.

TABLE 9

Wave length, in mμ	D	E	Wave length, in mμ	D	E
428	0.46	4600	533	0.24	2400
436	0.455	4550	574	0.12	1200
465	0.50	5000	619	0.075	750
496	0.46	4000	665	0.04	400

SUMMARY

1. α-Furyldioxime is suitable for the determination of small amounts of nickel.

2. The capacity of nickel α-furyldioxime to give colored solutions in organic solvents can be used as the basis of a very sensitive colorimetric method for the determination of small amounts of nickel.

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A METHOD FOR THE QUANTITATIVE DETERMINATION OF THE ESTERS OF PHENYLCARBAMIC ACID

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In recent years organic compounds have been finding more and more uses in various branches of agriculture. In particular, the esters of phenylcarbamic acid are being used as selective herbicides for the destruction of weeds of the grass family and in young crops of dicotyledonous plants [1, 2]. This group of compounds is also recommended for the treatment of root crops in order to restrict their growth during long storage [3, 4]. Such compounds are usually used in agriculture as powders (dusts) which are ground mixtures of the esters of phenylcarbamic acid with some inert filler (talc, kaolin, pyrophilite). These compounds can also be employed as aqueous suspensions, which are prepared by stirring up the requisite powders with water.

Despite the practical use of the esters of phenylcarbamic acid, there are no methods described in the literature for their quantitative determination in various products. Only qualitative reactions are described for some of the esters of phenylcarbamic acid [5], while it has been suggested that they be determined quantitatively on the basis of their nitrogen content [6].

Very recently a method has been described for the determination of isopropyl phenylcarbamate [6], based on its decomposition with a mixture of sulfuric acid and phosphoric acid on heating. Under these conditions the isopropyl ester is quantitatively broken down to give CO_2, which is then determined by absorption in standard alkali.

It is obvious that such a method could not be applied for the quantitative determination of phenylcarbamic esters in preparations which contain any other products capable of evolving CO_2 in acid solution.

In connection with what has been said above we carried out a number of investigations on methods for the quantitative determination of phenylcarbamic esters. We first studied the determination of the esters by titration of the aniline formed during alkaline or acid hydrolysis of the carbamate with sodium nitrite

$$C_6H_5NHCOOR + 2NaOH \rightarrow C_6H_5NH_2 + Na_2CO_3 + ROH;$$

$$C_6H_5NHCOOR + HCl + H_2O \rightarrow C_6H_5NH_2HCl + CO_2 + ROH.$$

We studied this method for the ethyl and isopropyl esters of phenylcarbamic acid. For analysis, ethyl phenylcarbamate, with m.p. 52°, and isopropyl phenylcarbamate, m.p. 90°, were employed.

As a result of these experiments it was established that aniline is quantitatively released on hydrolysis of the methyl and ethyl ester of phenylcarbamic acid with KOH in aqueous-alcohol solution. This reaction is complete in 2 hours. The isopropyl phenylcarbamate is not hydrolyzed at all under these conditions.

Complete hydrolysis of isopropyl phenylcarbamate is achieved by boiling it with concentrated HCl.

On the basis of these results we can recommend the following procedure for the quantitative determination of ethyl phenylcarbamate.

An aliquot of the test material containing approximately 0.6-0.7 g of ethyl phenylcarbamate is weighed into a 100 ml round bottom flask fitted with a reflux condenser. 10 ml of a 20% aqueous solution of KOH in 25 ml of 96° ethyl alcohol is then added to the flask, and the whole boiled for 2 hours.

When hydrolysis is complete, the reaction mixture is quantitatively transferred to a 500 ml conical flask. The round-bottom flask and the reflux condenser are carefully rinsed with 150 ml of distilled water, and the washings combined with the solution in the conical flask. The contents of the flask are then neutralized with HCl until the solution is acid to Congo red and then 20 ml of concentrated HCl (sp.gr. 1.16) added in excess, along with 10 ml of a 10% aqueous solution of KBr. The mixture thus obtained is titrated against 0.1 N $NaNO_2$ at 15-20°. The end point is determined by the appearance of a stable color for starch-iodide paper when a drop of the titrated solution is placed upon it after the solution has stood for 5 minutes. A blank experiment is carried out, in which 0.1 N $NaNO_2$ is titrated against a mixture of 25 ml 96% alcohol, 10 ml 20% KOH, and 150 ml distilled water, which has been neutralized to Congo red, and 10 ml excess concentrated HCl added.

The percentage of ethyl diphenylcarbamate is calculated from the formula $\frac{(a - a_1)K \cdot 165}{b \cdot 100} = \%$, where a – is the number of ml of 0.1 N $NaNO_2$ with a correction factor K used for titrating the sample, a_1 – the number of mls of 0.1 N $NaNO_2$ with a correction factor K used for titrating the blank; and b is the weight of sample taken.

Results for experiments on the determination of ethyl phenylcarbamate, as such, and in dusting powders, are given in Table 1.

TABLE 1

No.	Weight of sample (b)	0.1 N $NaNO_2$ in ml (a)	0.1 N $NaNO_2$ in ml (a_1)	K	Compound, %
1	0.7004	41.53	0.62	1.034	99.65
2	0.5944	35.23	0.62	1.034	99.34
3	0.6132	36.42	0.62	1.034	99.61
4	0.7061	41.82	0.62	1.034	99.55
5	7[1]	41.57	0.62	1.034	9.98
6	7[1]	41.44	0.62	1.034	9.95
7	7[1]	41.51	0.62	1.034	9.97
8	7[1]	41.38	0.62	1.034	9.94

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1) A 10% dusting powder was used.

The results given in Table 1 for the analysis of ethyl phenylcarbamate show that the experimental error does not exceed normal analytical errors for the determination of amines by titration with $NaNO_2$ [7].

For the determination of isopropyl phenylcarbamate, the following procedure is recommended.

A weight of sample containing 0.4-0.5 g of isopropyl phenylcarbamate is weighed into a 250 ml round bottom flask fitted with a reflux condenser. 40 ml of HCl(sp.gr. 1.16) and 30 ml of distilled water are added, and the mixture boiled for 2 hours. When analyzing talc dusts, it is necessary to shake the flask frequently during the first 10-15 minutes of heating, because of the strong tendency of the reaction mixture to foam. This is the result of the formation of CO_2 during the decomposition of the carbonates contained in the talc.

When hydrolysis is complete, the contents of the flask are quantitatively transferred to a 500 ml conical flask. The round bottom flask and reflux condenser are carefully rinsed, and the washings combined with the hydrolysis liquor in the conical flask. 250 ml of water is used for washing out the flask and condenser. 15 ml of 10% aqueous KBr is then added to the contents, and the whole titrated against 0.1 N $NaNO_2$ at 15-20°. The end point is determined by means of starch-iodide paper, any color change being observed when a drop of the titrated mixture is placed on the paper after the solution has stood for 5 minutes. When the starch-iodide is colored the titration may be regarded as complete. A blank is carried out, in which 0.1 N $NaNO_2$ is titrated against a mixture of 40 ml HCl, 15 ml of 10% KBr, and 300 ml water.

The percentage of isopropyl phenylcarbamate is then given by $\frac{(a - a_1)K\cdot 179}{b\cdot 100} = \%$.

Results of some of the determinations are given in Table 2.

These results indicate that the error for an individual determination does not exceed the normal permissible errors for analyses of this type.

Equally good results were obtained for the analysis of isopropyl 3-chlorophenylcarbamate when the method described above for isopropyl phenylcarbamate was employed.

TABLE 2

No.	Weight of sample (b)	0.1 N $NaNO_2$ in ml (a)	0.1 N $NaNO_2$ in ml (a_1)	K	% of contents
1	0.4234	22.99	0.20	1.034	99.62
2	0.4240	23.08	0.20	1.034	99.88
3	0.4138	22.49	0.20	1.034	99.70
4	0.4320	23.49	0.20	1.034	99.78
5	0.4068	22.14	0.20	1.034	99.82
6	25 1)	23.03	0.20	1.034	1.690
7	25 1)	23.17	0.20	1.034	1.700
8	25 1)	23.00	0.20	1.034	1.690
9	25 1)	23.10	0.20	1.034	1.695

---

1) Dusting powder containing 1.7% isopropyl phenylcarbamate was analyzed.

SUMMARY

A method has been worked out for the quantitative determination of ethyl and isopropyl phenylcarbamates, respectively, which is suitable for their determination in various products used in agriculture.

The method is based on the quantitative liberation of aniline on hydrolysis of ethyl phenylcarbamate with alcoholic potash, and of isopropyl phenylcarbamate with concentrated HCl, and the subsequent titration of the aniline with sodium nitrite.

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THE USE OF DIMEDON FOR SPOT TESTS FOR ALDEHYDES

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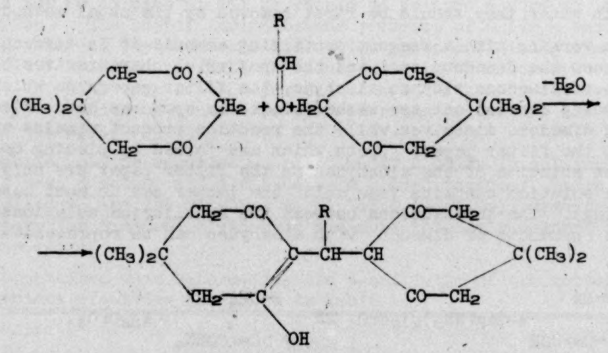
A large number of spot tests have been suggested for the detection of aldehydes; nevertheless, none of these is specific, nor does any allow aldehydes to be detected with certainty in the presence of ketones [1, 2].

In recent years the so-called dimedone, or 5,5-dimethylcyclohexane-1,3-dione, has found increasing application for the detection of aldehydes. Since this reagent reacts with ketones only under exceptional conditions, it may be regarded as a specific reagent for aldehydes [3]. The condensation products of dimedone with aldehydes are colorless; consequently, dimedone has not been used for spot tests for aldehydes.

Reactions between aldehydes and dimedone proceed as follows:



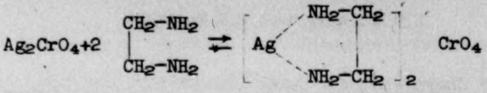
Thanks to the enol character of the compounds formed, they are fairly acidic; in particular they dissolve in dilute alkalis. This property of the condensation products of dimedone with aldehydes can be used for spot tests for aldehydes. It must be borne in mind, however, that dimedone itself possesses acidic properties, but, in contrast to its condensation products with aldehydes, dimedon is fairly soluble in water.

We have shown in our experiments that indicators for the saturation method cannot be used for detecting the acid character of the reaction products between dimedone and aldehydes.

Not very long ago it was proposed that equilibrium systems formed by dissolving silver chromate in ammonia or ethylenediamine solutions [4] could be used for the detection of the acid character of compounds of low solubility.

On adding a small amount of a compound which can combine with ammonia or ethylenediamine to form a salt-like, or complex compound, this equilibrium is destroyed and silver chromate, which is red-brown in color, is precipitated. The condensation products of dimedone and aldehydes which have a low solubility can produce this effect.

$$\text{I.}\quad Ag_2CrO_4 + 4NH_3 \rightleftarrows [Ag(NH_3)_2]_2CrO_4$$

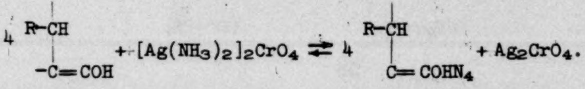
II.


$$Ag_2CrO_4 + 2\begin{array}{l}CH_2-NH_2\\ |\\ CH_2-NH_2\end{array} \rightleftarrows \left[Ag\begin{array}{l}NH_2-CH_2\\ \quad\quad\ |\\ NH_2-CH_2\end{array}\right]_2 CrO_4$$

Preliminary experiments showed that both the above equilibrium systems liberate silver chromate as the result of the absorption of ammonia or ethylenediamine under the influence of the condensation products of dimedone with aldehydes. If a drop of a solution of dimedon saturated in the dcold is placed on a filter paper, and subsequently a drop of an aqueous or aqueous-alcoholic solution of an aldehyde placed on the spot thus formed, then on drying, the spot will be colored a reddish brown under the influence of the drop of reagent solution. The behavior of the dimedone itself depends on the reagent used; on soaking with a solution containing ammonia, the spot containing the dimedone is colored a brown color, while a solution containing ethylenediamine colors the spot containing the dimedone a light yellowish-brown color.

By means of this method, aldehydes can be detected even in the presence of acids which are fairly soluble in water. If acids are present which have a very low solubility in water, they should be first removed by the usual methods.

Since, when working with a reagent containing ammonia it is difficult to distinguish between the dimedone spot and the spot which characterizes the reaction product of dimedone with an aldehyde, the filter papers on which the spot tests are being carried out are washed after the spot has been dried; when this is done the dimedone dissolves, while the reaction product remains at a definite spot on the filter paper. Spots which are formed by placing control drops of the test solution of the aldehydes on the filter paper are only colored when the initial solution contains free acid (the latter can in most cases be removed by washing). The interactions between the equilibrium solutions of the condensation products of dimedon with aldehydes can be represented by the scheme:



$$4\begin{array}{l}\quad\ \ |\\ R-CH\\ \quad\ \ |\\ -C=COH\end{array} + [Ag(NH_3)_2]_2CrO_4 \rightleftarrows 4\begin{array}{l}\quad\ \ |\\ R-CH\\ \quad |\\ C=COHN_4\end{array} + Ag_2CrO_4.$$

We tested a number of aldehydes (in the form of their 2.5% aqueous or aqueous-alcohol solutions) for their capacity to give the reaction considered. It was shown that formaldehyde, cinnamic aldehyde, o-, m-, and p-hydroxybenzaldehyde, p-nitrobenzaldehyde, valeric aldehyde, anisaldehyde, benzaldehyde, β-hydroxynaphthoic aldehyde, piperonal, citral, and furfural all give positive reactions.

Below we give the procedure adopted for the detection of aldehydes by means of equilibrium ammonia and ethylenediamine solutions of silver chromate, respectively.

Detection of Aldehydes By Means of An Equilibrium Ammoniacal Solution of Silver Chromate

Reagents Necessary

1. Dimedone solution. Dimedone is dissolved in boiling water, and after

cooling the solution is filtered.

2. Equilibrium solution. Freshly precipitated and washed silver chromate is shaken for 10 minutes with an approximately 1% solution of ammonia (after shaking, some silver chromate should still remain undissolved). The solution is filtered or centrifuged, and the filtrate kept in a dark cupboard in a bottle with a ground glass stopper. Completely clear solutions must be used for any tests (if any precipitate separates out on storage, it is filtered again).

Reaction Procedure

Eight points are drawn on a filter paper (one half of an ashless paper) with a pencil. Two drops of dimedone solution are placed on two of the points by means of a capillary (control dimedone drops); on four of the other points a drop of dimedone and a drop of the aldehyde test solution are placed successively. Two drops of the aldehyde test solution are placed on the two remaining spots (aldehyde control spots). The moist spots are dried over a heated wire gauze to dryness, and the filter paper immersed for 30 seconds in a water bath heated to 30°. On removal from the water bath, the paper is rapidly washed with a stream of distilled water and then dried between two sheets of filter paper. On the still-damp paper where the spots are, drops of reagent solution are placed. When this is done the control dimedone spots should remain colorless or be colored a weak brown color (an intense color for the dimedone spots indicate that the test has not been carried out correctly); the control aldehyde spots should not be colored at all, or should be colored a more or less intense brown-red color. (The latter indicates the presence of a large amount of acid insoluble in water in the test solution). The spots containing dimedone and the test solution in the presence of aldehydes will be colored an intense red-brown color, in which very often a periodic character can be observed which indicates that a series of concentric colored rings or sectors are formed on the periphery of the spot.

The reaction may be regarded as positive if a color is obtained at those points where both dimedone and aldehyde were placed together, while the spots where only dimedone and the aldehyde were placed separately remains colorless, or if the spots for dimedone + aldehyde are more intensely colored than the control spots alone.

Results obtained when determining the sensitivity of the method described above for various aldehydes are given in Table 1.

TABLE 1
Sensitivity of the Reaction for Detecting Certain Aldehydes Using Dimedone and an Equilibrium Ammoniacal Solution of Silver Chromate

Aldehyde	Sensitivity, in μg	Limiting Dilution
Formaldehyde [1]	1	1:2000
Citral	4	1:500
β-Hydroxynaphthoic aldehyde	25	1:80
Valeric aldehyde	50	1:40
m-Hydroxybenzaldehyde	50	1:40
Cinnamic aldehyde	60	1:33
Furfural	2000	1:10

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1) Formaldehyde was dissolved in water; all the other aldehydes were dissolved in alcohol-water mixtures.

The large sensitivity range is obviously related to differences in the solubility of the condensation products of the aldehydes with dimedone. The low sensitivity to furfural in all probability is related to the incomplete condensation with dimedone under the experimental conditions employed.

Detection of Aldehydes by Means of an Ethylenediamine Equilibrium Solution of Silver Chromate

Reagents Necessary

1. Dimedon solution. Prepared as indicated above.
2. Equilibrium solution. Prepared as indicated above except that a 1% sol solution of ethylenediamine is substituted for the ammonia solution.

Experimental Procedure

Control and test spots were made on a filter paper as described above.

Drops of reagent solution are placed on the dried paper (without washing) at the points marked on the paper. When this is done the control dimedone spots are colored a light brown; the color of the control aldehyde spots is determined by the amount of acids in the test solution. Usually they are a light yellow color. The color of the test spots is a blood-red or reddish-brown; sometimes the color appears in the form of rings or sectors. The difference in color is particularly clear when the paper has been dried. When this is done, the control spots become a grey-yellow color, while the color of the test spots does not change.

It should be noted that in the case of formaldehyde the test spots turn completely black after 8-10 minutes, while the spots given by the other aldehydes do not change appreciably in the course of many hours. The black color is explained by the separation of metallic silver; the silver however, is not formed as the result of a "photochemical" reaction, since it appears in the dark as well as in the light.

The results given in Table 2 illustrate the sensitivity of the reactions described.

TABLE 2

Sensitivity of Reactions for Detecting Certain Aldehydes Using Dimedone and an Equilibrium Solution of Silver Chromate in Ethylenediamine

Aldehydes	Sensitivity, in μg	Limiting Dilution
Formaldehyde	1	1:2000
Valeric aldehyde	2	1:1000
p-Hydroxybenzaldehyde	2.5	1:800
Citral	3	1:665
β-Hydroxynaphthoic aldehyde	3	1:665
Cinnamic aldehyde	5	1:400
Piperonal	50	1:40
Furfural	2000	1:10

The results show that the sensitivity of the ethylenediamine reagent is higher than that of the ammoniacal one, which confirms the suggestion advanced above that the solubility of the condensation product of an aldehyde with dimedone affects the sensitivity.

The method can be applied for the detection of aldehydes in actual organic analysis.

1. Detection of Formaldehyde in Methyl Alcohol. The reaction described above is carried out on a filter paper using methyl alcohol as the test solution.

3-4 g of formaldehyde can be detected in the alcohol.

2. Detection of Methyl Alcohol in Acetone. The method is based on the oxidation of methyl alcohol to formaldehyde and the detection of the latter. 3-4 drops of the test acetone are placed in a quartz micro-tube, and some cupric oxide introduced on a knife point. The tube is fitted with a capillary outlet, the other end leading into another tube containing a drop of water. Starting from the top end of the copper layer and gradually working down, the quartz micro-tube is heated with a micro-burner in the course of 3-5 minutes until all the tube has been heated. By means of a capillary, a drop of the water used for absorption is placed on a prepared filter paper and the presence of aldehyde tested for. The reaction is very clear-cut with technical acetone. Chemically pure acetone does not give the reaction.

3. Detection of Glycerol in Aqueous Solutions. The method is based on the conversion of glycerol to acrolein and the detection of the latter. The test is carried out in the micro-apparatus described above, sodium bisulfate being used instead of cupric oxide. A definite, positive reaction is given by one drop of a 1% solution of aqueous glycerol.

4. Detection of Vanillin in Vanilla. A few milligrams of finely ground vanilla are heated for 1-2 minutes in a micro-test tube with 3-5 drops of aldehyde-free ethyl alcohol. A drop of the solution obtained is tested for aldehyde as before. A clear-cut result is given.

5. Detection of Aldehydes in Catalyzate Liquids. During the contact transformation of certain organic substances, aldehydes are often formed, but their detection by existing methods is extremely difficult, though essential. The method described enables this problem to be solved too.

In particular we succeeded in detecting aldehydes in the water and catalyzate[1] obtained when normal hexyl alcohol is passed over commercial molybdenum catalysts at 550°. A distinct aldehyde reaction was given by the 115-145° fraction, while the other fractions gave negative results.

SUMMARY

1. A dimedon reaction is proposed as a spot test for aldehyes. The reaction is based on the use of the acidic properties of the enol compound formed as a result of the reaction of dimedon with aldehydes.

2. The reagent used for these condensation products are equilibrium ammoniacal and ethylenediamine solutions, respectively, of silver chromate.

3. Examples of the practical application of these reactions are given.

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[3] V.S.Johnson, R.D.Shenan and R.A.Reid, "Organic Reagents for Organic Analysis", Russian translation, Foreign Literature Press, 1948.

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Received July 17, 1950.

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1) The experiments were carried out at the Department for the Chemical Treatment of Oil and Gas, of the Saratov University, by Malakhova. The head of this Department is Docent R.D.Obolentsev.

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CRITICISM

M.V.Shchigol and N.B.Burchinskaya's article on the "Quantitative Determination of Trivalent Iron by Means of Tetraborate" (J. Anal. Chem. 7, 289, 1952.)[1]

Considerable attention has been devoted in the Soviet Press to the need and significance of criticism and self-criticism in various fields of activity. The article mentioned above shows that without a self-critical attitude on the part of the research worker towards the method which he employs, the experimental work can lead to errors on the part of both research worker and reader.

As the basis of their work M.B.Shchigol and N.B.Burchinskaya, studied the potentiometric titration of trivalent iron salts with sodium tetraborate. On the basis of their observation, the authors deducedthe existence of various complex iron borates.

The potentiometric method for investigating complex formation is of great importance. Striking examples of the application and development of this method are to be found in the work of the school of Greenberg and others. In Shchigol and Burchinskaya's work, however, coarse experimental errors are made and it is easy to show that the conclusions which they have drawn are worthless. In order to confirm that the cations of trivalent iron and the anions of boric acid form a complex in solution, it is necessary to show that these ions actually link up. When the potentiometric method is used, proof of this nature may be obtained if the electrodes which are used as the indicator have a potential which depends in a definite way on the concentration of one of the reacting ions. An electrode which has this property with respect to Fe^{3+} would be, e.g., platinum in a solution containing both ferrous and ferric ions; with respect to the borate anion, a suitable electrode would be any metal covered with a layer of the practically insoluble borate of the metal. The application of each of these electrodes would require additional investigation under the given conditions. The theory of indicator electrodes is expounded in all text-books on potentiometric analysis, in courses on electro-chemistry, etc. The authors of this article however, did not even take the elementary basis of the theory of potentiometric analysis into account. They used platinum covered with platinum black as the indicator electrode. This is not a completely suitable type of hydrogen electrode, and its potential depends primarily on the hydrogen ion concentration. Ferric salts and salts of boric acid are known to be strongly hydrolyzed in aqueous solution. Therefore when one solution is titrated against another, there will be a change in hydrogen concentration which will be completely independent of whether complex iron borates are formed during titration or not. At best, even under experimental conditions it would be difficult to achieve in practice, one might be able to make only very limited and indirect conclusions. Shchigol and Burchinskaya however measure potentials (which depend as said above on hydrogen ion concentration), draw curves, and from the peaks on these curves "conclude" that complexes are formed, and write their formulas.

Moreover the authors adduce values for the instability constants of these complex iron borates. These values might find their way into reference books and into actual practice, since they are published in a responsible journal, while in actual fact these constants have an even more insecure basis than the "fact" of complex formation. For any calculations of the instability constants it is essential that the equilibrium concentrations of the components be known, including the concentration of the borate ion. In order to find this concentration, the concentration of borate not combined as a complex must be known.

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[1] See Consultants Bureau English Translation, page 325 ff.

(the authors just did not determine this), as well as the pH of the solution (which they also ommitted), and the acid dissociation constant of boric acid. The results available in the literature for this last constant are not very accurate, the question of the state of the boric acid in solution is very complex, and the constants change considerably with concentration. In most cases it is generally accepted that the anion of pyroboric acid ($B_4O_7^{2-}$) does not exist in dilute aqueous solutions, being converted under these conditions (as a result of hydration) into more simple forms - the metaborate or orthoborate ions. Thus, neither the expression "instability complex" of the tetraborate complexes of iron, nor the numerical values adduced by the authors of the article under discussion, have any foundation whatsoever.

Among other serious errors in the method adopted, the following must be mentioned. It has been repeatedly requested that any articles which include the results of measurements also include the chief primary results from which it might be possible to get some idea of the probable accuracy of the method and to adjudge the results. In the article considered, the values of the potentials themselves are not given, just the values of $\Delta E/\Delta V$. At the same time, e.g., from Fig. 1 it can be seen that, in all, only 1.5 ml of borax solution was used while 24 measurements of potential were made. From these results also, and from the text on the same page, it is obvious that the titrations were made dropwise (volume of ca. 0.06 ml). On the basis of these 24 points (1 drop at a time) a curve has been drawn in which there are, in the authors' opinion, 5 (five!) peaks, and from which they deduce the existence of 5 complexes of varying composition. A number of equations are written, the physical meaning of which in most cases cannot be interpreted, or related to the titrations. Formulas for multi-nuclear compounds are adduced, etc. The inadmissibility of such a method of experimentation and the complete unreliability of the conclusions drawn are obvious, even if the measurements of the potentials could give any basis for postulating the formation of complexes.

On the first page of the article under discussion, it is stated that "One drop in excess of borax after the equivalence point leads to the formation of a precipitate, obviously as the result of the break-down of a complex". It is well known, however, that excess of a coordinating ion usually leads to the formation of more stable complexes (c.f. the effect of excess KCN, sodium salicylate, sodium oxalate etc., on the salts of iron and of a number of other metals). Moreover, the authors' "conclusions" contradict one of their own conclusions re the instability constant. From the expression for the instability constant, it follows that an increase in the concentration of borate ions should lead to a firmer binding of the iron into a complex[1].

Fig. 3 is designated "the cryoscopy of the system $FeCl_3 - Na_2B_4O_7$". It has been shown in a number of articles by Yu.A.Fialkov that the cryoscopic method can be a valuable method for the study of complex formation in solution. M.V.Shchigol and N.B.Burchinskaya however, ignore the elementary rules for evaluating the accuracy of the results and the method of observation. On the basis of 17 observations they draw a curve with 7 (seven!) breaks; from the tables and the curve, the existence of 2 minima are deduced which "confirm the formation of the iron borates $FeB_4O_7^+$ and $Fe_2(B_4O_7)$" in solution". The most elementary considerations shows that one minimum which corresponds to the ratio

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[1] The most probable hypothesis, on the basis of the authors' observations relative to the formation of a precipitate on addition of excess borate, is as follows: in the first stages, apparently, it is not a complex that is formed, but a colloidal solution of a basic salt which coagulates on addition of excess borate, as a consequence of a sharp change in thepH of the solution.

$FeCl_3 : Na_2B_4O_7 = 2 : 3$ could, however, be explained by the formation of hydroxides (or basic salts) of iron, and consequently does not by any means confirm the formation of a complex. The authors have nothing to say on how or why the second minimum arises. If the usual hypothesis for the relation between the lowering of the freezing point and electrolyte concentration is applied, the existence of the second minimum cannot in general be explained, so that it cannot confirm anything except the lack of attention paid by the authors to their experimental method.

The number of such examples can be increased considerably. We shall only state what is obvious to any analytical chemist, viz., that the potentiometric titration of iron with borax (with the necessity of determining the free acid) is of no practical use. Though we should like to help comrades M.B.Shchigol and N.B.Burchinskaya to eliminate the drawbacks in their work and to use their experimental results, we cannot see any possibility of doing so. The drawbacks do not just refer to individual sections of the work; the whole method as such is unsound.

From what has been said the following conclusions can be drawn. This work before printing represents at best a large amount of fruitless work. After printing[1] however it can only be harmful, since it sanctions the application of completely inadmissible apparatus and seeks to introduce very poor quality material into the fund of scientific knowledge. This impels us to make the present observations. The editorial board is also to blame, since, had it examined the work more carefully, it would at least have spotted without much trouble that the indicator electrode being used was the wrong one.

A.K.Babko

Received November 10, 1952.

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1) M.M.Shchigol and N.B.Burchinskaya's report was discussed at a session of the Analytical Section of the Kiev Branch of the Mendeleev Society on 4/11/1952. The authors were unable to give clear-cut answers to observations made by a number of comrades including the author of the present criticism.

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The All-Union Scientific Research Institute for Chemical Reagents, M.Kh.P. has synthesized a new, highly sensitive, organic reagent for magnesium – Magneson IREA. Organizations and departments wishing to test the new reagent can obtain a free sample, together with instructions for its use, upon request to the Institute (Moscow, 33, Samokatnayl ul.d.4-a). Requests should be entered as soon as possible, so that production of the new reagent can be controlled.

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HIGH FREQUENCY TITRATION

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I

Many articles appeared in recent years which have been devoted to a new volumetric method – the method of high frequency titration (at current frequencies of the order of megacycles). This method is essentially the same as conductometric titration, but in contrast to the latter, observations of changes in the electrical characteristics of the solution during high frequency titration (H.F. titration) are made by enclosing the vessel containing the titration solution within the current circuit, so that there is no need for electrodes to be placed inside the solution, instead, they are placed outside the vessel in direct contact with the walls (external electrodes). By means of this method which is also very accurate, it is possible to widen the scope of volumetric analysis.

Just like conductometric titration, H. F. titration is possible because the electrical resistance of a solution varies with the electrolyte in solution and with the concentration of the electrolyte. However, during H.F. titration, in contrast to the usual conductometric titrations, the changes in the capacity component of the total electrolyte resistance are also of essential significance. For H.F. titrations the electrodes are placed outside the vessel since the resistance of the vessel itself does not present an essential barrier to the passage of the current at the frequencies employed.

Changes in the resistance and capacity of the dielectric–viz., the solution with changing composition – are measured by methods normally used in radio-technics. A detailed analysis of the apparatus described in the literature for H.F. titration will be given below.

A large number of articles has been devoted to the application of H.F. titration in analysis, which include reviews such as those of Blake [1], Haedel and Malmstadt [2], and Hall [3]. A systematic review of H.F. titrations appears in the German journal of analytical chemistry [4,5].

In addition to H.F. titration itself, which is discussed below in detail, H. F. methods have already found a variety of uses. Thus, long before the appearance of foreign papers on this question, Troitsky [6], used measurements of the dielectric constants obtained by means of a H.F. generator for separating the adsorption zones of colorless compounds during chromatographic analysis. Other papers have been devoted to the same purpose [7,8]. By means of a H.F. generator it is possible to determine the percentage of water in alcohol in a matter of seconds with an accuracy of ±0.05% for a 1% weight concentration of water [9]. A change in the concentration of KCl in benzene can be determined for concentrations of the order of 0.0006% [10]. H.F. set-ups have been used for studying the kinetics of chemical reactions in solutions [11,12] and for investigating metallic complex salts [13]. The measurement of the dielectric constants by means of H.F. was used by the Soviet radio amateur Velichko [16], for an important practical purpose – the rapid determination of grain moisture.

The application of H. F. apparatus for titration is of comparatively recent origin [15,10]. It has been shown that the accuracy of H.F. titrations in most cases is not less than, and in many cases exceeds that of usual analytical methods. Thus, normal acid-base titration can be carried out using a H.F. generator in 3-4 minutes, with the same accuracy [15,16,17, et al] as the potentiometric titration method. Weak acids with dissociation constants of the order of 10^{-7} [18], can be titrated with a fair degree of accuracy

By means of a 350-megacycle generator it was found possible to titrate silver nitrate with 0.1 M sodium chloride when the total concentration of electrolyte consisted of 10 mole % of silver nitrate and 90 mole % sodium nitrate at the beginning of titration [19]. The total concentration of electrolyte at the end was equivalent to 0.2 M approximately. Normal conductometric titration would be impossible in practice if such an amount of an inert electrolyte ($NaNO_3$) was present. The titration curves for this case are shown in Fig. 1. Readings of the registering instrument are plotted along the ordinate, against the amount of reagent added in mls along the abscissa. The Fig. shows that all the points lie on two straight lines intersecting at a point which corresponds to the end point. In the same article titration curves for mercuric nitrate with potassium thiocyanate, and of oxalic acid with thorium nitrate are also given. The error in each case does not exceed 0.2%.

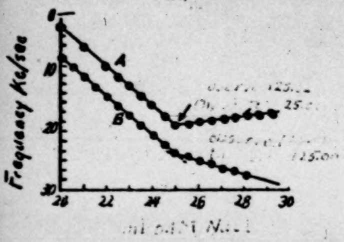

Fig. 1.

H.F. titration enables small amounts of thorium to be determined in the presence of zirconium and titanium with an error of not more than ± 1.2% [20], and enables water hardness to be determined [21], with results for the calcium content which are better than those obtained by the standard method used in America. The chloride ion can be determined with a high degree of accuracy (an error of only 0.2%) by precipitation with mercury salts in 0.00004-0.003 M HCl [22]; the error of a potentiometric method for such a system is 2%, while that of the conductometric method is 1.5%. H.F. titration gives good results for the determination of sulfur in sea water and in gasoline products. 0.01-0.0001 N SO_4^{2-} solutions can be titrated in the presence of H_2O_2 with an error of ± 2.2% [23]. (0.09 – 6.72 mg of sulfur can be determined). H.F. generators with frequencies of 20 megacycles can be used for the volumetric titration of beryllium with ammonium phosphate, NaOH, or ammonium hydroxide [24]. The error for the determination of 10-40 mg of beryllium in the presence of excess HCl is on an average equal to ± 0.7%. There was no satisfactory method for the volumetric determination of beryllium before the advent of the H.F. method.

In addition to the neutralization and precipitation reactions described, H.F. analysis can also be used for oxidation-reduction titrations [10 2], and for reactions accompanied by the formation of soluble complexes.

From the review given above it is clear that H.F. titrations can give analytical results on a par with gravimetric methods (0.0 n %) and sometimes better than the latter. Another advantage of the new method of titration is its speed, which depends only on the velocity of the reaction used for analysis in solution, and the good reproducibility of the results.

The general form of the curve obtained during H.F. titration is reminiscent of those obtained during conductometric titration. (See Fig.1). The curves obtained during H.F. titration are usually linear near the equivalence point, nevertheless, even when there are deviations from linearity, they do not lower the accuracy of the method.

It has been suggested recently that in cases where the final end point is not very clearly defined during H.F. titration a differential method could be used [25]. When this method is used, the reagent is added to the solution being titrated at a constant rate. The apparatus automatically registers both the direct changes in the electrical characteristics of the solution during the titration process (the frequency changes) and the velocity with which they change (i.e. the change of frequency in unit time). The differential method gives a sharper end point so that, e.g. even small amounts of CO_3^{2-} can be detected in NaOH.

The method described, however, has its limitations. The main drawback is the total concentration of the titrated solution. The maximum sensitivity of the H.F. titration method will depend both on the nature of the coupling between the titration vessel and the generator circuit (this will be considered in detail below) and on the composition of the solution. Thus for H.F. titration with a 30 megacycle generator (by the beat method) the maximum sensitivity for the determination of HCl concentration in solution is given for concentrations of HCl of the order of 0.003 N, while for sodium chloride the maximum sensitivity is given for concentrations of 0.014 N [2,26]. In this range the charge in concentration can be determined with an accuracy of 0.05%. If titration is carried out in which measurements of current of voltage are involved, then working at the same frequency and with the same apparatus there are two regions of maximum sensitivity:for sodium chloride these are −0.0005 −0.01 N and 0.05 −1.0 N. Here the changes in sodium chloride concentration can be determined with an accuracy of 0.5%. The greater the equivalent conductivity of the solution, the narrower the concentration range (thus, the range is narrower for HCl than for NaCl). Nevertheless, titrations are very often carried out in analytical chemistry where the electrolyte concentration exceeds 1 M. When solutions of higher concentration are titrated, it becomes necessary to increase the frequency of the current used for titration. In particular, it was for concentrations of the order of about 1 M that a H.F. apparatus operating at 350 megacycles was constructed [19].

II

It has already been stated that it is the changes in the electrical characteristics of the solution with changes in concentration that are used in H.F. titrations.

Any solution considered as a dielectric can be characterized by three independent constants: 1) the dielectric permeability (ϵ); 2) the magnetic permeability (μ), which is practically constant for solutions of electrolytes, and 3) the specific conductivity or specific resistance which is determined by the value of the total H.F. losses in the dielectric. For electrolytes, the specific resistance and the dielectric constant at radio frequencies depend on the concentration of the solution and on the current frequency [27].

In order that in our review of the methods proposed in the literature we may differentiate that which is characteristic for, and on which H.F. titration is based, from the usual radio technical set ups [28] which are not specific in the given instance, we shall introduce the concept of the "electric cell" (donor).

Thus, any H.F. titration apparatus consists of an electric cell and a measuring set up, the chief component of which is the H.F. generator.

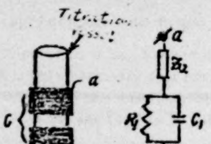

Fig. 2.

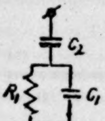

Fig. 3.

Electrical cells of type "C". If a vessel containing an electrolyte is placed in a H.F. field, e.g. in a condenser, then the equivalent electrical circuit of the cell may be represented as shown in Fig. 2 [3]. Here R_1 and C_1 are the resistance and capacity of the electrolyte itself, respectively, while Z_2 is the total resistance of the condenser, the plates of which are formed on the one hand by the electrodes, and on the other by the surface of the liquid at the vessel walls, the walls of the vessel acting in this case as the dielectric. Resistance R_1 and capacity C_1 are proportional to the specific resistance and the dielectric permeability of the electrolyte, these in turn depend on the geometrical dimensions of the vessel and the condenser plates and also on the concentration and the nature of the solution. R_1 and C_1 could be determined directly, if the condenser plates were arranged on the inside surfaces of the vessel walls, i.e., if the plates were in contact with the electrolyte. At the frequencies used in H.F. titration however R_1 and C_1 differ from the R_1 and C_1 obtained for the same solutions when D.C. or low frequency A.C. are used, because of a decrease in relaxation force with increasing frequency [27]. During titration, the frequency changes only insignificantly within limits such that R_1 and C_1 for a given solution are practically independent of frequency changes. Z_2 can be measured by any of the methods used for measuring small capacities with low losses, e.g., by means of a Q-meter, the meter surface of the vessel walls having been preliminarily covered with a silver layer or the vessel filled with mercury. At the frequencies employed in H.F. titration the losses in the glass of the titration vessel can be neglected. Therefore the equivalent circuit Fig. 2 can be simplified [26,29 30]. The simplified circuit is shown in Fig.3.

Only the terminals ab (Fig.3) are accessible for measurement during H.F. titration. Having measured the total resistance Z of the circuit over the terminals ab, we can determine the values of R_1 and C_1. During H.F. titration it is not the absolute values of the resistances R_1 and capacity C_1 that are determined, but the way in which the total resistance of the circuit Z changes with the concentration changes of the solution. It is important therefore that changes in R_1 and C_1 should effect the strongest possible changes in the total resistance Z, so that it is essential to choose the correct ratio between the resistance of capacity C_2 and the total resistance of branch R_1C_1.

The total resistance of the circuit shown in Fig.3 will be:

$$Z = \frac{1}{j\omega C_2} + \frac{1}{\frac{1}{R_1} + j\omega C_1} = \frac{R_1}{1+(\omega C_1 R_1)^2} - j\left[\frac{\omega C_1 R_1^2}{1+(\omega C_1 R_1)^2} + \frac{1}{\omega C_2}\right], \quad (1)$$

where $\omega = 2\pi f$, the angular frequency (f = the current frequency).

From this formula it is clear that the active component of the total resistance

$$R = \frac{R_1}{1+(\omega C_1 R_1)^2} \quad (2)$$

which is most strongly dependent on changes in R_1, when

$$(\omega C_1 R_1)^2 \ll 1. \quad (3)$$

When

$$(\omega C_1 R_1)^2 \gg 1, \quad (4)$$

R is strongly dependent not only on R_1 but also on C_1.

When condition (3) is satisfied the reactive component of the total resistance

$$X = \frac{\omega C_1 R_1^2}{1+(\omega C_1 R_1)^2} + \frac{1}{\omega C_2} \quad (5)$$

will be most strongly dependent on R_1 and C_1. When condition (4) is satisfied X depends only on C_1.

In practice it can happen that during titration R_1 decreases while C_1 increases or vice-versa. In such a case it is only necessary that conditions (3) and (4) be satisfied where R depends only on R_1 while X depends only on C_1. In this case non-fulfilment of the given conditions will decrease the sensitivity of titration. Conditions (3) and (4) can be fulfilled by choosing the operating frequency ω and the value of the condenser C.

Electrical cells of type "C" have been used in a number of investigations using H.F. titration (see e.g. [1 16 31 32]).

Electrical cells of type "L". In the previous section dealing with the equivalent circuits for C-cells we developed to some extent the theories re cells of this type already current in the literature [3,25,26,30,31]. No analysis of the L-type cell has hitherto been given, and no equivalent circuits of a coil with a suitable vessel for titration have been given anywhere.

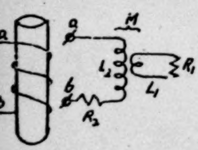

Fig. 4.

An "L" type cell is characterized by the fact that the vessel containing the electrolyte is made the core of a H.F. self induction coil. The simplified equivalent circuit for this case is given in Fig. 4. Here L_2 is the inductance and R_2 is the resistance of a coil when the titration vessel containing no electrolyte is placed in it. L_1 and R_1 are the corresponding inductance and resistance which are characteristic of the solution.

For a given frequency the inductance $\underline{L}$ is determined only by the geometrical dimensions of the titration vessel; it increases with increase in the ratio $\underline{D/l}$ where D is the diameter of the vessel and $\underline{l}$ - the height to which it is filled with electrolyte at that part which is located in the high frequency field of the coil; R_1 — is proportional to the specific resistance of the electrolyte. L_1 and L_2 are the mutual inductances where the coefficient of mutual inductance is $M = \underline{k}\sqrt{L_1 L_2}$, where $\underline{k}$ is the coupling coefficient; $\underline{k}$ is greater the greater the volume of coil occupied by electrolyte; $\underline{k}$ is always less than one.

The circuit in Fig. 4 can be transformed into the circuit shown in Fig. 5.

In this circuit $L_{int.}$ and $R_{int.}$ are the inductance and resistance introduced into the coil circuit when the titration vessel is filled with electrolyte. From the theory of coupled circuits [33], it is known that the resistances introduced are determined by the following formulas :

$$R_{int.} = \frac{\omega^2 M^2}{R_1^2 + \omega^2 L_1^2} R_1 = \frac{k^2 \omega L_2}{1 + \left(\frac{R_1}{\omega L_1}\right)^2} \left(\frac{R_1}{\omega L_1}\right). \tag{6}$$

$$L_{int.} = -\frac{\omega^2 M^2}{R_1^2 + \omega^2 L_1^2} L_1 = -\frac{k^2 L_2}{1 + \left(\frac{R_1}{\omega L_1}\right)^2} \tag{7}$$

Let us introduce the dimensionless quantity $\underline{Q} = \frac{\omega L_1}{R_1}$ by which we shall characterize the solution in future.

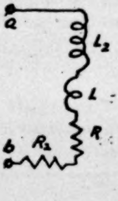

Fig. 5

The physical meaning of the quantity Q which is called the quality can be made clear by means of the following considerations: let us multiply both the numerator and denominator of the expression for $\underline{Q}$ by $I_m^2/2$ and substitute $(2\pi/\underline{T})$ for ω. Here I_m is the amplitude of the H.F. current, while $\underline{T}$ is the period of the H.F. oscillation. Then

$$Q = \frac{2\pi \frac{L I_m^2}{2}}{\frac{R I_m^2}{2} T}$$

i.e. the quality is directly proportional to the amplitude value of the energy in the coil and is inversely proportional to the energy loss in the coil for one period at high frequency. By characterizing the solution by the value $\underline{Q}$; it is possible to express $R_{int.}$ and $L_{int.}$ in terms of $\underline{Q}$.

$$R_{int.} = \frac{k^2 \omega L_2}{1 + Q_1^2} Q_1 \tag{8}$$

$$L_{int.} = -\frac{k^2 L_2 Q_1^2}{1 + Q_1^2} . \tag{9}$$

The quality of the coil without any electrolyte in the titration vessel will be $Q_2 = \frac{\omega L_2}{R_2}$ and with electrolyte

$$Q_1 = \frac{\omega(L_2 + L_{int.})}{R_2 + R_{int.}} = Q_2 \frac{1 + Q_1^2 (1 - k^2)}{1 + Q_1^2 \cdot 1 + \left(\frac{k^2 Q_2}{Q_1}\right)} \tag{10}$$

The value of $\underline{k}$ which depends on the geometrical dimensions of the coil and the titration vessel can be determined easily by means of a simple experiment. If the inner surface of the vessel is silvered then Q_1 will be so much greater than unity that it may be accepted that $Q_1^2 \gg 1$ when

$$L_{int.} = -\frac{k^2 L_2}{1 + \frac{1}{Q_1^2}} \approx -k^2 L_2. \tag{11}$$

Thus, having measured the inductance L_2' of the coil containing a silvered titration vessel and the inductance L_2 of the coil with a vessel which has not been silvered, we can find the coupling coefficient:

$$k = \sqrt{\frac{L_2 - L_2'}{L_2}} = \sqrt{1 - \frac{L_2'}{L_2}} \qquad (12)$$

If the vessel is filled with electrolyte and the quality of the coil Q is measured, then by means of equation (10) it is possible to find the numerical value of Q_1.

The applicability of the method of measurement chosen for the titration depends on the order of the value of Q. Thus, if $Q_1 < 1$ the measuring set-up will be most sensitive to changes in $L_{int.}$. If $Q_1 > 1$, however, the most effective method of measurement will be that using a Q-meter (vide infra).

The application of the L-cell is described in a number of papers [10, 17, 21, 34].

Cells of the simple types have been described above. In principle it should be possible to use cells of a mixed type (LC-cells).

III.

All the measuring apparatus used for registering changes in the electrolyte characteristics during H.F. titration can be divided into a number of groups according to the principles on which they are based:

1) Z-meters are used for following changes in total resistance $\bar{Z}$. 2) Q-meters are used for measuring changes in high frequency power losses in oscillating generator circuits. 3) F-meters are used for measuring changes in frequency. 4) apparatus of a mixed type.

1) Z-meters [26, 31]. If a resistance $\bar{Z}_{cell}$ is in series with the cell resistance $\bar{Z}_1$ and the e.m.f. is $\bar{U}$ then the current will be given by

$$\bar{I} = \frac{\bar{U}}{\bar{Z}_{cell} + \bar{Z}_1} . \qquad (13)$$

The current $\bar{I}$ will also change when $\bar{Z}_{cell}$ changes. Changes in I can be followed during titration. A simplified scheme of the principal parts of such an apparatus is shown in Fig. 6. A C-cell is used in this type of apparatus [15], while a galvanometer with a crystal detector is used for measuring the current.

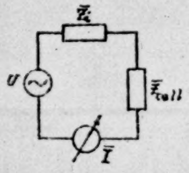

Fig. 6.

Blake [31] in his apparatus varied the sensitivity by changing Z_1 (the capacity of a variable condenser through which the cell is connected to the generator is varied). It would be expedient to keep $\bar{Z}_1$ a minimum and to vary the sensitivity by changing the voltage of the generator U. In this case a given sensitivity would be achieved for a minimum value of the current through the solution. (The current density passing through the electrolyte should not exceed 50-70 $\mu A/cm^2$, otherwise there will be appreciable heating of the electrolyte).

Since frequency changes do not affect $\bar{Z}_{cell}$ and $\bar{Z}_1$ appreciably, then the requirements for frequency stabilization of the H.F. generator are not very high in this method.

2. Q-meter set-ups can basically use either the principles on which the usual Q-meters are constructed [35] or the special type of operating conditions of a self-exciting generator, where the amplitude of the oscillations generated depends strictly on the "quality" of the oscillating circuit. The titration process in this case is followed by observing the changes in the anode or network currents of the generator. The maximum achievable accuracy of this method is determined basically by the stability of the generator voltage.

Apparatus with generators assembled according to a set-up using a two circuit auto-generator with a common cathode have been widely used [10, 16, 21, 32]. The amplitude of the oscillations in this case will be determined not only by the quality of the oscillating circuit in which the cell is included, but is also determined by the characteristic resonance frequency of this circuit f_r. This frequency f_r will change during titration (see F-meters). It is better to consider apparatus with generators of this type as being of the mixed type of apparatus. The accuracy of these apparatuses is basically determined by the stability of the voltage supply, since the amplitude of the oscillations generated in this case is strongly dependent on the operating conditions of the generator, and consequently both on anode and filament voltage respectively.

3) The apparatus most widely used is that based on the F-meter principle [11,17,19,22].

We have already noted that during titration, the cell which is connected directly to the generator circuit changes the characteristic resonance frequency of the circuit. Thus,

$$\frac{\Delta f}{f} = -\frac{1}{2}\left(\frac{\Delta C}{C} + \frac{\Delta L}{L}\right). \qquad (14)$$

where Δf is the frequency change of the generator circuit in which the cell is included; C and L are the total capacity and inductance of the circuit including the cell; ΔC and ΔL are the changes in the equivalent capacity and inductance of the cell during titration.

During H.F. titration the value of Δf/f is of the order of 10^{-3} and less, so that direct measurements of frequency changes are impossible. The heterodyne method is therefore used for measuring frequency changes during H.F. titration.

The gist of the method is as follows: the cell is included in the circuit of a self-exciting generator in such a way that the generated frequency is completely determined by the characteristic resonance frequency of the circuit f_0. During titration f_1 changes by an amount Δf so that it is possible to write $f_1 = f_0 + \Delta f$. The frequency f_1 of this generator is intermixed with the frequency of an auxiliary generator f_2 and the differential frequency $F = f_1 - f_2$ isolated. This differential frequency is measured directly by a frequency meter. Now the relative frequency changes will be considerably greater

$$\frac{\Delta f}{F} \gg \frac{\Delta f}{f_0}, \qquad (15)$$

since $F \ll f_0$ consequently these changes can be measured more accurately. The lower F, the lower the resolving power the frequency meter should have in order that it may have a given sensitivity. This differential frequency F could be chosen equal to zero, but for this purpose it would be necessary to eliminate the trapping of the frequency of one generator by the frequency of the other. Usually F is chosen to have a value of ca. 10^3 cycles since, under these conditions the coupling-hysteresis effect is not observed even when both generators are working on fundamental frequencies.

The heterodyne method is the most sensitive method and enables titration to be carried out with accuracies of the order of a tenth and even a hundredth of a per-cent. In this case it is very important that the generator have a highly stabilized frequency, since the latter determines the accuracy of the method.

The accuracy attainable at present by using H.F. methods of titrations is not final; even the results obtained to date however show the possibilities of this method. Moreover, the use of radio apparatus for H.F. titrations opens up great possibilities for the automatization of titration.

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THE USE OF DITHIZONE AS AN EXTRACTION INDICATOR

A. G. Karabash

In addition to numerous physico-chemical methods for indicating end points in volumetric analysis, chemical indicator-reagents have been successfully developed and improved for detecting equivalence points during titration; their advantage is simplicity and rapidity of titration [1].

The intensive development of precipitation and complex formation methods is characteristic of contemporary progress in volumetric analysis, particularly in the analysis of metals, including, in this connection the use of selective organic reagents which are recommended for qualitative analysis, (particularly in spot tests) for determining the equivalence point during titration.

Numerous examples of such new, internal or external indicators [2-12] can be quoted. Nevertheless it is only possible to note solitary attempts to search for indicators used universally for various methods of volumetric analysis.

A selective indicator is a selective reagent for a particular ionic or atomic group under the titration conditions used; the selectivity of its action just as for any other chemical reagent is related to the conditions of the reaction medium.

To a large extent highly sensitive selective indicators answer the requirements of direct rapid titrations,particularly for precipitation and complex formation methods.

The use of dithizone as a selective extraction indicator is considered below.

EXTRACTION INDICATORS AND THEIR USE

When chemical reagents are grouped according to their uses, in addition to internal and external indicators, it is rational to consider extraction indicators which are used during titration in the form of a solution in an immiscible solvent, in the layer of which all the indicator changes during titration can be followed, as an independent group.

In connection with this increasing use of organic reagents the characteristic technique of carrying out analytical operations particularly in the form of extraction techniques including the extraction indicator method, is also used more and more in practice.

Extraction indicators have been in use for a long time in inorganic analysis, e.g. solutions of iodine in organic solvents such as $CHCl_3$, CCl_4, C_6H_6, etc. have been used in iodometry [15-17]. Indication of the end point by iodine extraction is three times more sensitive than that of the iodine-starch reaction [18], and is applied very effectively in iodometric and iodatometric methods [18-23].

An extraction indicator method is used in neutralization methods for determination of pH, and for determining the equivalence point during titration, particularly in cases of cloudy or colored solution [24].

As examples of extraction indicator methods for reactions involving precipitation and complex formation the following may be quoted; fluorimetric determination, e.g. of aluminum with ferric thiocyanate in ether or alcohol layers as an indicator [25-27] the titration of ferric iron with ferrocyanide, using ferric thiocyanate in an isoamyl alcohol layer as indicator [28], the titration of zinc ferrocyanide and nickel cyanide using diphenylcarbazone in CCl_4 solution as indicator [29], the determination of picric acid and other orthopoly nitro phenols and picrates (Ca, K, nicotine, etc.) by means of methylene blue [30-32].

It should be noted that the little use made hitherto of extraction indicators in the practice of inorganic analysis does not correspond by any means to the possibilities of the method.

There is a great variety of extraction indicators. Sometimes the reacting substance is colored and is extracted in the solvent layer so that it can act as its own indicator, e.g. the solution of iodine in C_6H_6 or $CHCl_3$ in iodometry.

In the case of precipitation reactions and complex formation, a substance can be used as an extraction indicator, if it forms a compound (e.g. a complex) with the respective ion in solution, which can be distinguished by its color, and dissolves both in water and an immiscible organic solvent, the solubility being greater in the organic solvent. This last condition is satisfied when the distribution coefficient is favorable.

The extraction indicator is thus found predominantly in the layer of the organic solvent which is spatially separated from the sphere of action (the aqueous solution) by the surface of separation of the two liquid phases, but nevertheless through this same surface of separation the indicator is connected all the time via a mobile equilibrium with the reaction medium, and reflects all the changes which occur in the latter during titration. The first of these conditions, viz. the fact that the system consists of two phases distinguishes extraction indicators from internal indicators. The second condition, i.e. direct contact between indicator and reaction medium essentially distinguishes it from external indicators.

While possessing the characteristics of physico-chemical equilibrium conditions, extraction indicators in addition form a group which unites the essential features of the two other groups indicated above.

Extraction indicators are not so fast as internal indicators with respect to the speed with which equilibrium is attained; this speed can however be easily achieved by periodically shaking the solution during titration, thanks to the fact that the layer of organic solvent is broken up into small drops and to a significant increase in the surface of contact between the two liquid phases which results from the shaking.

The basic criteria which determine the practical value of an indicator are its selectivity (under the titration conditions) and sensitivity.

In this respect extraction indicators have the following advantages.

1. Localization of the indicator changes in the layer (or drop) of the immiscible organic solvent eliminates interference from the reaction medium and enables one to carry out observations more readily, e.g. in the case of turbid and colored solutions, and when titrating large volumes of dilute solutions.

2. The simplicity of regulating the sensitivity of the indicator within a wide range. This is effected by changing the ratio of the volume of the two liquid phases (water and the immiscible solvent), and the concentration of the indicator and its distribution coefficient in liquids which depends both on the character of the organic solvent and on the conditions in the titration solution (pH, etc.).

3. The possibility of using as indicators, new selective, highly sensitive organic reagents; particularly inner complex compounds, independently of the degree of their solubility in aqueous solutions.

In general the extraction technique is a very effective way of increasing the selectivity and sensitivity of analytical reactions and is widely used in colorimetric analysis for the determination of micro quantities [33].

It is natural to expect that the extraction method will find further applications for determining end points during titration.

THE PROPERTIES OF DITHIZONE AS AN EXTRACTION INDICATOR

Dithizone (diphenylthiocarbazone) is one of the most valuable organic reagents used for the analysis of metals, and a vast amount of work has been devoted to its practical application [33-43].

Dithizone behaves like a weak acid and forms salt-like inner complex salts with a number of metals of the H_2S and ammonium sulfide groups — the dithizonates are characterized by exceedingly bright colors, they are insoluble in water but dissolve readily in organic solvents.

In most of its reactions dithizone behaves as a mono-basic acid [41]. Two series of dithizones which differ in their stoichiometric ratios are known for some metals. The popular explanation of the structure of dithizone and of metallic dithizonates which postulates the existence of two tautomeric forms of the compounds — keto and enol — is not based on any experimental basis. In more recent papers it is assumed that the acid properties of dithizone are determined by the mercapto group contained in its molecule [43].

The dithizone complexes of many metals are very stable and according to the values of their instability constants they form a series similar to the sulfides [37,41,34].

The reactions of certain metals with dithizone are selective for certain definite experimental conditions which can be achieved by regulation of the pH of the solution and the use of various complexing agents for masking. The values of the molar extinction coefficients of dithizone ($\Sigma = 30{,}400$) and of the dithizonates ($\Sigma = 40{,}000-150{,}000$), respectively are considerably greater than that of the majority of organic dyes [41,37]. Dithizone reactions are accordingly characterized by high sensitivity. These properties of dithizone as a reagent are widely used in practice for qualitative analysis, and particularly for the quantitative determination of traces of many heavy metals by colorimetric methods, including colorimetric titration, and volumetrically for so-called extraction titrations. In the last instance, quantitative extraction of the metallic ions is carried out by means of dithizone which acts as the titration solution [in CCl_4, $CHCl_3$] [38,34].

Because of the solubility of the dithizonates and of dithizone itself, and because of the stoichiometric ratios which hold during these reactions, methods involving the use of dithizone are confined to the analysis of micro-amounts of metals (usually not more than ca. 100 μg).

Lead dithizonate (in solution in CCl_4 or $CHCl_3$) has been used as an indicator in neutralization methods for the determination of the acidity of dark colored liquids on titration with alkali [44,24].

In the methods described below dithizone in the form of its solutions in organic solvents has been used as an extraction indicator for volumetric methods involving precipitation and complex formation when ions of the H_2S group of metals participate [45]. During the titration of the metal cations with the respective precipitants or complexing agents (or during back titration) a small amount of the solution of dithizone in the organic solvent (CCl_4, $CHCl_3$, C_6H_6, toluene) which is immiscible with water is added to the aqueous solution of the salt and titration carried out with reagent solution, the latter being added in small amounts, the mixture being shaken after each addition and the color of the dithizone layer observed.

At or near the equivalence point as a result of precipitation or complex formation, there is a sharp increase or decrease in concentration of the reacting metal ion with corresponding decomposition or formation of the dithizonate of the metal which is accompanied by a sudden change in color of the organic solvent.

Since free dithizone in CCl_4 (or $CHCl_3$, etc.) has a very intense emerald-green color, while the metal dithizonates have extremely bright and characteristic colors, under suitable titration conditions the equivalence point can be determined very accurately. This indication of the end point is based on the difference in value of the instability constants of the metal dithizonates and the instability constants or solubility products (activities) of the complex of these metals with the complexing agents or precipitants used; this difference in the values of these constants can, if required, be changed by regulating the conditions of the reaction medium (pH, addition of masking agents, etc.)

In actuality, when considering the reversible equilibrium between the two-phase system and the titration reaction, (precipitation or complex formation in the simplest case) [37, 41] the ratio of the two colored forms of the indicator in the organic solvent layer at the equivalence point may be expressed as follows.

$$\frac{[ND]_{or}}{[MD]_{or}} = \frac{K'_{MD}[H^+]}{K_{ND}[M^+]_{e.p.}} = \frac{K'_{MD}[H^+][A^-]_{e.p.}}{K'_{ND}PR_{MA}} = \frac{K'_{MD}[H^+]}{K'_{ND}\sqrt{PR_{MA}}}$$

The legends used are as follows. ND – dithizone, which is represented as a monobasic acid with an anion D^-, M^+ – the cation of a univalent metal M; A^- – the anion which forms a difficultly soluble (or complex) compound MA with metal M; MD – the dithizonates of the metal M, K'_{ND} and K'_{MD} – constants which take into account the total equilibrium of dithizone (ND) and dithizonate (MD), which include both the dissociation constants in aqueous solution and the corresponding distribution coefficients of the undissociated molecules between the two liquid phases [37,41] PR_{MA} – the solubility product of the compound MA.

The figures in square brackets represent the corresponding concentrations.

Thus, the choice of optimum titration conditions can be made not only empirically but also on the basis of the results of the chemical equilibrium.

A favorable ratio for the equilibrium constants indicated above under the respective medium conditions enables dithizone to be used as an extraction indicator in volumetric analysis; e.g., in argentometry, cyanometry, mercurimetry, in precipitation by sulfides and in other methods involving precipitation and complex formation, as described below.

Method Used for Titration

An aliquot of the aqueous test solution is placed in a test tube of ca. 20 ml ($\phi = 15$ mm) or 50 ml ($\phi = 20$ mm) capacity fitted with a ground glass stopper, and a ca 0.0001 M or even weaker (0.00005 M) solution of dithizone in CCl_4($CHCl_3$, C_6H_6) in amounts of ca. 1/20 – 1/10 of the volume of the aqueous solution added. Titration is carried out at room temperature (not higher than 25°) with a solution of the reagent from a buret graduated in 0.02 ml).

The reagent is added in small amounts, the solution being shaken after each addition (the test tube is stoppered) and the color of the dithizone layer observed.

Initially, the color of the indicator layer which changes on addition of the reagent, rapidly reverts to its original color on gentle shaking. Towards the end of the titration, the color changes are a bit slower and it is necessary to shake for 5-10 seconds.

The end of the titration is that point at which there is a clear-cut change in the dithizone color in the CCl_4 layer which does not disappear on further shaking of the liquid for ca. 30 seconds and which is characteristic of the formation or decomposition of the respective dithizonates of the reacting metal. In order to be certain that the end point has been reached, an excess of 1-2 drops of reagent is added which is not taken into account.

One titration takes about 5-7 minutes.

The reagent solution is standardized with the respective standard solution under identical conditions (concentration, volume and composition of the solution), or the reagent solution is made up using a known weight of reagent.

The following notes may also be necessary.

1. During titration it is essential that the optimum conditions for the given method must be maintained, particularly the pH of the solution. Addition of alkali or acid must be carried out accurately.

2. The indicator solution of dithizone in CCl_4 (or $CHCl_3$ C_6H_6) is prepared in the usual way, observing all the conditions when working with dithizone (screening it from heat and light in a dark, covered bottle.)

The dithizone preparation may be given a preliminary purification if necessary by successive extractions from ammoniacal and sulfuric acid solution.

3. The molarity of the dithizone solution can be checked if necessary by an extraction titration with standard silver solution.

It is recommended that the sensitivity of the indicator solution be checked under identical conditions to those used for titration, i.e., the indicator error which is usually negligible, is determined, although it must only be taken into account when doing micro-determinations.

4. The sensitivity of the dithizone indicator solution for the various cases (macro, micro, and semi-micro) during titration can be regulated by varying the amount used and its concentration in the organic solvent.

For the titration of dilute solutions and also for micro-determinations, the minimum amount of dithizone indicator solution is used (as weak as possible, e.g., 0.00005 M) while the reagent used for the titration should not be too weak.

5. Oxidizing agents such as Fe^{3+}, oxides of nitrogen, and others, must be absent in the titration solution. HNO_3 can be allowed. If other metals are present (i.e., different from those being determined), then the extraction of their dithizonates in the indicator layer must be taken into account.

TABLE 1

Titration of Silver with a Solution of Iodide, and the Argentometric Determination of Iodide using Dithizone as an Extraction Indicator

Number	Used for titration: H_2SO_4 dilute (1:3), in ml	water in ml	$8\cdot10^{-5}$ solution of dithizone in CCl_4, in ml	0.025 M $AgNO_3$, in ml	0.025 M KI used in ml	Concentration of acid in equivalents N H_2SO_4
1	0.5	3.5	0.5	1.00	1.02	0.8
3	3.0	1.0	0.5	1.00	1.00	4.6
6	1.0	4.0	1.0*	2.00	2.00	1.0
7	2.5	2.5	1.0	2.00	2.00	2.6
11	5.0	–	1.0	5.00	5.00	3.1
14	15.0	–	2.0	10.00	10.01	4.0
	0.1N HNO_3		solution of 0.5 % eosin			Fajans titration
17	0.5	3	0.1	2.00	2.00	
19	0.5	3	0.1	5.00	5.00	
	H_2SO_4 dilute (1:3) in ml		$8\cdot10^{-5}$ M solution of dithizone in CCl_4, in ml	0.025 M KI in ml	0.025M $AgNO_3$, in ml	
21	2.5	2.5	1.0	2.00	2.00	2.6
23	3.0	1.0	1.0	3.00	3.00	2.8
	H_2SO_4 dilute (1:3) in ml		$5\cdot10^{-5}$ M solution of dithizone in CCl_4, in ml	0.0025 M $AgNO_3$, in ml	0.0025 M KI, in ml	
26	1.0	1.0	0.4	0.50	0.50	3.1
27	1.0	1.0	0.4	1.00	1.00	2.3
29	1.0	0.5	0.4	2.00	2.01	1.7
30	2.0	1.0	0.4	3.00	3.00	2.0

Description of the Methods Used

1. Determination of the Silver Ion Ag^+

a) By titration with the I^- ion. Titration of 0.01 N or more dilute solutions (down to 0.001 N) with KI is carried out in H_2SO_4 solution within the limits 1.0-9.0 N H_2SO_4 (acid dilution by volume 1:30-1:3), the optimum acidity being 3-4 N H_2SO_4. The indicator solution used is a $1\cdot10^{-4}$-$5\cdot10^{-6}$ M solution of dithizone in CCl_4 (or in C_6H_6, toluene, etc.)

The change in indicator color at the equivalence point is very sharp (0.01 ml of a solution of 0.002 M KI is enough to produce a change), from a canary-yellow to an emerald-green.

The results obtained by this method are in exact agreement with titrations of Ag^+ with KI using Fajans method with eosin as an adsorption indicator, but the end point given by dithizone is considerably more sensitive than that of eosin. The results, both micro and semi-micro, are given in Table 1.

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* In experiment No. 6 the indicator was a solution of dithizone in benzene.

TABLE 2

The Titration of Silver with Solutions of Bromides and Thiocyanates, and the Argentometric Determination of Bromides and Thiocyanates using Dithizone as an Extraction Indicator

Number	Used for Titration				Amount of solution used, in ml	Concentration of acid N, H_2SO_4, in equivalents
	H_2SO_4 dilute (1:3) in ml	Water (ml)	$1 \cdot 10^{-4}$ M solution of dithizone in CCl_4 in ml	0.025 M $AgNO_3$ in ml		
					0.025 M KBr	
2	2.0	2.0	0.5	1.00	1.00	3.1
4	5.0	–	1.0	2.00	2.00	5.1
6	5.0	–	1.0	3.00	3.01	4.2
					0.025 M KCNS	
8	2.5	1.0	0.5	1.00	1.01	4.2
9	3.0	1.0	0.5	1.00	1.00	4.6
11	5.0	1.25	1.0*	2.00	2.00	4.5
16	15.0	–	2.0	10.00	10.01	3.9

b) By titration with Br^-. Titration with 0.01 N KBr is carried out in H_2SO_4 solution at an acidity of not less than 2N H_2SO_4; the optimum is ca. 4N H_2SO_4 (dilution 1:9 by volume).

The end point is determined with dithizone as described above. The results are given in Table 2.

c) By titration with CNS^-. Titration with 0.01 N KCNS is carried out in not less than 3.5 N H_2SO_4; optimum 5-6 N H_2SO_4 (i.e., at a dilution of 1:6 by volume).

The end point is determined with dithizone, as described above. The results are given in Table 2.

2. Determinations of I^-, Br^-, and CNS^- by Titration with Ag^+

These determinations are carried out under the conditions described above.

3. Determination of Cl^-.

This can be done indirectly by a back titration of excess $AgNO_3$ with KI after filtering off the AgCl precipitate.

4. Determination of CN^-.

Two variants of the argentometric method for cyanides were investigated.

a) Titration of the cyanide in a weakly alkaline solution (0.3-0.6 N NH_4OH or 0.1-0.2 N NaOH) with $AgNO_3$, using a 0.01% solution of dithizone in CCl_4 as indicator.

At the end point the aqueous solution, which has up to this point a weak yellow color, acquires a reddish-rose color, while on slight shaking the yellowish layer of the CCl_4 solution changes to a violet-red color.

The change in color of the indicator layer during extraction titration is very sharp— 0.02 ml of 0.025 N $AgNO_3$ being sufficient to effect the change. When a small excess of $AgNO_3$ is added a bulky, flocculent, violet-red precipitate of silver dithizonate floats on the surface of the CCl_4 layer.

Silver can be titrated in this way with a solution of cyanide. When this is done the silver dithizonate, which is only very slightly soluble in CCl_4, transfers its weak yellow color to the CCl_4 layer; in this case an indication of the end point is given by the flotation of the violet-red precipitate of dithizonate in equilibrium in the CCl_4 layer or on the surface separating the CCl_4 and water layers. On the other hand, silver dithizonate dissolves readily in chloroform, imparting to it an intense yellow color. Therefore, if a ca. 0.01% solution of dithizone in $CHCl_3$ is used as an indicator in the cyanide titration outlined above, the weak yellowish color of the $CHCl_3$ layer changes sharply to a canary-yellow at the end point.

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* In experiment No. 11 the dithizone was dissolved in toluene.

TABLE 3

The Argentometric Titration of Cyanides Using Dithizone as an Extraction Indicator

Number	Taken for titration				Ml of 0.025 M $AgNO_3$ used	Notes
	NH_4OH 10% in ml	Water, in ml	$1 \cdot 10^{-4}$ M solution of dithizone in CCl_4, in ml	~0.05 M KCN, in ml		
1	0.5	4.0	1.0	1.00	1.02	
3	0.7	3.0	1.0	2.00	2.04	In experiments 1-10 the indicator was dithizone in CCl_4
6	1.0	–	1.5	5.00	5.05	
	2N NaOH					
8	0.3	3.0	1.0	2.00	2.05	
10	0.5	1.0	1.5	5.00	5.03	
	NH_4OH, 10% in ml		0.3 M KI, in ml			
12	0.5	3.0	0.2	2.00	2.04	Denizh titration
15	0.5	–	0.2	5.00	5.03	
	NH_4OH, 10%, in ml		$1 \cdot 10^{-4}$ M solution of dithizone in $CHCl_3$, ml	0.050 M KCN in ml		
16	0.3	5.0	1.0	1.00	1.00	In experiments 16-26 the indicator was lead dithizonate in $CHCl_3$; 0.05 ml of 0.025 M $Pb(NO_3)_2$ was preliminarily added to all the solutions.
20	0.5	4.0	1.0	2.00	1.99	
21	0.5	3.0	1.5	3.00	2.98	
23	0.8	1.0	2.0	5.00	4.95	
24	0.8	1.0	2.0	5.00	4.96	
26	1.0	1.0	3.0	10.00	9.93	
			0.2 M KI, in ml			
27	0.5	3.0	0.2	3.00	2.98	Denizh titration
29	0.5	3.0	0.2	2.00	1.99	

b. By the use of a solution of lead dithizonate in chloroform as an extraction indicator.

The titration is carried out under the same conditions as for the first variant. To a weak alkaline solution (0 3-0.6 N NH_4OH) of cyanide is added one drop of 0.025 M $Pb(NO_3)_2$, and then 1-2 ml of 0.01% dithizone in $CHCl_3$. After shaking, the $CHCl_3$ layer acquires a carmine-red color because of the lead dithizonate dissolved in it.

During titration, the white precipitate of silver cyanide which forms on addition of $AgNO_3$ dissolves on mixing. The end point, which is a sharp change in the $CHCl_3$ layer from carmine-red to a canary-yellow, is determined by the formation of silver dithizonate on the appearance of a very small excess of Ag^+ ions in the solution (from 0.01-0.02 ml of 0.025 N $AgNO_3$).

Because of large differences in the instability constant of lead and silver dithizonate, respectively, a clear-cut selective extraction of the silver dithizonate with the $CHCl_3$ occurs. A back titration can be done in the same way. Both variants (a) and (b) gave identical results.

During the argentometric determination of cyanides by the second variant (b) it was established that the presence of a small amount of Zn in the test solution (in molar ratios $ZnSO_4$: KCN = 1:5) does not affect the results.

The presence of $[K_4Fe(CN)_6]$ in solution under the conditions described above does not interfere with the determination of CN^- either.

TABLE 4

Titration of Mercuric Salts with Iodide Using Dithizone as an Extraction Indicator

Number	Taken for titration: Concentrated H_2SO_4 (in ml)	Water (in ml)	$1 \cdot 10^{-4}$ M solution of dithizone in CCl_4, (in ml)	Standard solution of ca. 0.0125 M $HgSO_4$ (in ml)	Ml of 0.025 KI used	Concentration of acid N-H_2SO_4
1	1.0	2.0	1.0	1.00	0.98	7.4
7	1.0	4.0	1.5*	1.00	0.98	5.3
3	1.25	3.75	1.5	2.00	1.95	5.1
6	2.5	2.5	2.0	2.00	1.96	10.2
	H_2SO_4 dilute (1:3), in ml				0.025 M KI, in ml	
8	2.5	–	0.5	0.10	0.97	6.5
10	2.5	–	0.5	0.10	0.96	6.5
11	2.0	–	0.5	0.050	0.48	7.3
12	2.5	–	0.5	0.050	0.49	7.5

In parallel with the methods described above, the test solution of cyanides was also titrated with $AgNO_3$, using the Liebig-Denizh method with KI as an indicator (turbidimetric). Indicator correction in this case amounted to 0.02 ml of 0.025 N $AgNO_3$.

The results obtained are in good agreement with previous ones (vide Table 3). As compared with the Liebig-Denizh method, however, the argentometric determination of cyanide by means of dithizone as the extraction indicator has the advantage of being more convenient, and also enables the end point to be determined more accurately, particularly in the second variant, when lead dithizonate is used.

5. The Determination of Hg^{2+} by Titration with I^-

The titration of 0.02-0.002 M solutions of mercuric salts with KI is carried out in H_2SO_4 solution at a dilution of H_2SO_4 : H_2O (by volume) of not less than 1:4, the optimum being ca. 1:3 (but not more than 1:2).

The change in color of the dithizone layer (in CCl_4 or C_6H_6) from orange-yellow to dark red is very sharp, 0.01-0.02 ml of 0.002 M KI being sufficient to effect the change (vide Table 4).

The end point corresponds to the equation:

$$Hg^{2+} + 2I^- \longrightarrow HgI_2$$

6. The Determination of Gold Au^{3+} by Titration with Thiosulfate

The titration of auric chloride in 0.5-1.0 M solution of HCl saturated with chloride (KCl, NaCl) is carried out with a 0.01-0.002 N solution of $Na_2S_2O_3$, using a ca. 0.01% solution of dithizone in CCl_4 (Table 5).

In the saturated solution of chloride (KCl, NaCl) the layer of gold dithizonate in the CCl_4 is intensely colored a gold-yellow, which changes into an emerald-green on addition of a small excess of $Na_2S_2O_3$.

7. Determination of Heavy Metals by Titration with Sulfide (Na_2S)

a) Titration of Pb^{2+} and of Cd^{2+} is effected with a solution of 0.01-0.005 M Na_2S in neutral solution in the presence of boric acid (H_3BO_3).

The change of color of indicator – a solution of dithizone in benzene – is very sharp from a light red to an emerald green.

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* In Experiment 7 the indicator used was dithizone in benzene.

TABLE 5

Titration of Gold with Thiosulfate Using Dithizone as an Extraction Indicator

Number	Taken for Titration					Ml of 0.009575 N $Na_2S_2O_3$, in ml
	solution of 10% HCl, in ml	water, in ml	KCl crystallization	$1 \cdot 10^{-4}$ M solution of dithizone in CCl_4, in ml	Au^{3+} µg	
1	1.0	3.0	to saturation	1.0	500	0.57
3	1.0	2.0	"	1.0	1000	1.16
6	1.0	1.0	"	1.0	1500	1.75
						0.002 N $Na_2S_2O_3$, in ml.
8	1.0	1.0	"	0.3	100	0.55
11	1.0	1.0	"	0.3	250	1.36
13	2.0	1.0	"	0.3	500	2.73

TABLE 6

Titration of Hg, Ag, Pb, Bi, Cd with Na_2S and the Determination of Sulfide Sulfur (S_2) by Titration with the Salts of These Metals Using Dithizone as an Extraction Indicator

Number	Taken for Titration				Reagent solution used in ml
	H_2SO_4 concentration in ml	water in ml	$1 \cdot 10^{-4}$ M solution of dithizone in C_6H_6 in ml	Test solution in ml	
				0.0125M $HgSO_4$	Na_2 solution
3	0.7	2.3	2	2.00	2.79
4	0.5	2.5	2	2.00	2.80
				Na_2S solution	0.0125 M $HgSO_4$
7	0.3	1.7	2	3.00	2.05
8	0.3	1.7	2	3.00	2.06
				0.025 M $AgNO_3$	Na_2S solution
10	0.3	4.2	2	0.50	0.73
12	0.8	3.2	2	1.00	1.48
				Na_2S solution	0.025M $AgNO_3$
13	0.3	2.7	2	2.00	1.30
14	0.3	2.7	2	2.00	1.32
	H_2SO_4 (1:3)			Na_2S solution	0.0025M $HgSO_4$
15	0.2	–	0.5	1.00	0.74
16	0.2	–	0.3	1.00	0.74
17	0.2	–	0.5	2.00	1.48
	H_3PO_4 in g			0.025 M $Pb(NO_3)_2$	Na_2S solution
19	0.5	2.0	0.5	0.10	0.40
23	1.0	3.0	1.5	0.30	1.20
	H_3PO_4 in g			0.025 $CdCl_2$ in ml	Na_2S solution
25	0.5	1.0	0.5	0.10	0.40
28	1.0	1.5	1.0	0.20	0.80
30	1.0	1.5	1.0	0.30	1.20
	$NaHCO_3$ in g			0.01 M $Bi(NO_3)_3$	Na_2S solution
31	0.5	2.0	1.5	0.20	0.52
32	0.5	2.0	1.0	0.20	0.52
33	0.5	2.0	1.5 CCl_4	0.40	1.04

b) Bi^{3+} is titrated with 0.005 M Na_2S in the presence of sodium bicarbonate. The change in color of the dithizone in benzene or CCl_4 indicator is very sharp from orange-yellow to emerald-green.

c) Hg^{2+} and Ag^+ are titrated with a 0.01 M solution of Na_2S in a weak H_2SO_4 medium.

The change in color of the dithizone in benzene indicator is very sharp from an orange (Hg^{2+}) or canary yellow (Ag^+) to emerald green.

8. **Determination of Sulfide Sulfur (S^{2-} Ions) by Titration with Solutions of Heavy Metal Salts** was carried out under similar conditions using a solution of dithizone in benzene or CCl_4 as indicator.

Results for the determinations of the metals ions and of sulfide sulfur are given in Table 6.

The results given in Tables 1-6 are typical of the large number of experiments (1500 volumetric determinations were made altogether). The results obtained using dithizone as an extraction indicator are characterized by their reproducibility and high accuracy.

SUMMARY

1. The characteristics of extraction indicator methods are considered.

2. Dithizone (diphenylthiocarbazone) has been used as an extraction indicator for volumetric analysis in methods involving precipitation and complex formation in which metals of the H_2S group participate.

The method is based on the formation or decomposition of metallic dithizonates at the titration end point, which is accompanied by a sharp change in the color of the organic solvent layer (CCl_4, $CHCl_3$, C_6H_6).

3. The series of experiments carried out show the expediency of using dithizone as an extraction indicator in the following methods for the determination of ions:

argentometry $-Ag^+$, I^-, Br^-, CNS^-;
cyanometry $-Ag^+$, CN^-
mercurimetry $-$ Hg^{2+}, I^-
precipitation with sulfides $-$ Hg^{2+}, Ag^+, Pb^{2+}, Bi^{3+}, Cd^{2+}, S^{2-};
determination of Au^{3+} with $S_2O_3^{2-}$.

The optimum conditions for the medium (pH of the solution) favorable to the accurate titration of each of the ions indicated above have been worked out.

In these methods, from the point of view of selectivity, high sensitivity and accuracy of results, dithizone excels the usual external indicators recommended in classical methods.

4. The respective macro-, micro- and semi-micro methods were used.

For the latter the use of dithizone as extraction indicator is of particular interest.

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THERMAL ANALYSIS WITH REGISTRATION OF THE VOLUME OF GAS EVOLVED

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Thermal analysis involving registration of the heating curves on a Kurnakov [1] pyrometer, and the use of simple and differential temperature recorders (thermograph) has been widely used [2]. This method of analysis gives the phase characteristics of the component parts of a complex mixture, as a result of which it has proved essential for investigations of various metals and alloys, minerals, rocks and ores. Recently it has become possible to apply the thermograph for quantitative phase analysis as well, by measuring the reading of the differential recorder with a planimeter. [3]

Many of the thermal effects revealed by the thermograms are related to gas evolution processes. Measurement of the volume of the gases evolved can be a new and effective method for quantitative phase analysis [4] which is more accurate than the thermographic method, and should find wide application. The most expedient means of realizing this method is the automatic registration of the volume of gas at the same time as the temperature curves are recorded on a Kurnakov pyrometer.

The requirements for registering gas evolution processes led us to construct an apparatus [5] which works on the principle of measuring the resistance of a platinum (or nichrome) wire stretched along the axis of a gas buret filled with mercury. The amount of mercury which flows into the communicating vessel depends on the volume of gas entering the buret, so that the acting length of the wire increases. The resistance of the wire is measured with a resistance bridge balanced at its middle. A mirror galvanometer giving direct readings on photographic paper fixed to the drum of a Kurnakov pyrometer serves as the indicator.

The drawback of the apparatus which has been described before was that the mercury flowing from the buret created a gas pressure in the buret which differed from atmospheric pressure, and varied during the experiment; this necessitated introducing corrections or carrying out special graduations for each reaction vessel and led to considerable irregularity in the volume scale on the photogram obtained. Moreover, in a number of cases a change in pressure from normal is not admissible.

The self-compensating buret which is of a new design (see plate, page 213) is free from these draw-backs. Automatic compensation of the mercury in buret A and in the communicating vessel (B) is realized by moving B up or down by means of motor (E) which can rotate either way. The motor is controlled through a system of relays when contact is established via the auxiliary mercury manometer (C) connected to the buret. When the pressure in the buret (and in the manometer) increases or decreases as a result of gas coming in or going out respectively, the compensating vessel containing the mercury is lowered or elevated until normal pressure is again established in the buret.

The apparatus is mounted on a wooden board (180 x 900 mm) and is fixed vertically on four nails embedded on the main side. On the outside surface the following items are fixed: a 100-ml glass buret, a manometer, a three-way tap, and the compensating vessel containing mercury, suspended on a cat-gut from the motor pulley. Clamps are also fitted on this die for switches (F) and indicators. All the electrical set-up is mounted on the back surface of the board which is 12 cm from the wall.

Three contacts are introduced into the U-shaped manometer; the middle and right hand side contacts are fused directly into the glass. The other side contact is regulated; it is fused into the glass tube inserted into the left limb of the manometer. The amount of mercury poured into the manometer is such that there is only a small gap between its surface and the side contacts. The smallest change in pressure in the buret leads to a rise of mercury in one of the manometer limbs to the contact, as a result of which the cathode circuit of the electronic relay is closed.

The twin relay is mounted on the base of a radio transformer FLS-2 with a converted setting. The relay consists of two parts working independently of each other, one comes into action when the left hand container of the manometer is closed, while the other operates when the right hand contacts of the manometer are closed. The anode current which thereupon comes into action operates the corresponding electromagnetic relay of a telephone type which switches on the current in one of the wires of the electric motor (for clockwise or anti-clockwise rotation). The electronic relays work on 6P3 of 6F6 tubes. An electrolytic condenser is included in parallel to avoid jarring the telephone relay.

In this set-up a universal 12 V electric motor with reducing gear was used (clockwise or anti-clockwise rotation). In order to supply the motor a winding was added to the transformer to give 12 V, and to ensure a current of 2 A*. In addition to the relay the motor can be brought into action by means of press buttons, one of which ensures a clockwise rotation and the other the reverse.

Release switches are fitted below the motor pulley, through the forks a thread passes, on which the leveling vessel is suspended. During the upward motion to the extreme position a knot on the thread pushes the form of one of the release switches and shuts off the current even when the relay or press buttons are still switched on. This prevents accidents which can occur if the vessel containing the mercury tightens on the rotating pulley. The other release switch (not shown in the diagram) acts when the buret is at its lowest point.

G, H and I on Figure 1 represent the drum, motor and pyrometer illuminator respectively.

The resistance bridge is assembled on a small, ordinary strip of thin Getinax. The resistances are wound from manganin or constantan wire. All the contacts are soldered with tin.** The bridge is fed from a 4-6 V accumulator or with a rectified grid current. If the latter is used a stabilizer must be used since voltage variation distorts the photograms. The stabilized main voltage is stepped down to 4-6 volts as indicated on the diagram by means of a separate transformer and is rectified by means of a selenium rectifier. An accumulator, however, gives better results. An additional resistance can be included in series with the mirror galvanometer according to its sensitivity. Accurate regulation which enables the volume to be registered on the photographic paper is realized by using a variable resistance R_6.

Thermal analysis involving registration of the volume of gas evolved requires some special apparatus. Heating the test material in the usual open crucibles is impossible in this case. Though only a small amount of material is used (0.1-0.2g) the clearness of the thermographic registration is not less than when normal amounts (2-5 g) are used; in fact the accuracy increases significantly, since the time which each process takes decreases and the heat inertia also decreases. Thus, on the records of processes in which large amount of material are used, e.g., the dissociation of dolomite (t = 760°) is partially superimposed on the decomposition process of calcite (t = 900°), while when small amounts are used these two effects are clearly distinguishable because of the rapidity of heating (Figures 2 and 3).

The sample (just like a standard for the differential thermo-couple) is placed in a quartz (or, for temperatures below 600°, heat-resistant glass) 30 x 5 mm micro-tube. The micro-tube 1 with the sample is placed in the reaction vessel 2 shown in Figure 4. A thermo-couple in a porcelain tube 8 is introduced into the same place. A glass nozzle 6, smeared with grease is fitted on the end of the thermocouple tube to ensure that the lead from the thermocouples is hermetically sealed, while a rubber collar hermetically joins the thermo-couple tube with the reaction vessel. The latter is made of quartz or heat-resistant glass. The micro-tube plus standard and differential thermocouples are placed in a long narrow tube made from the same material as the reaction vessel; this need not necessarily be hermetically sealed. The widened part 3 of the tube is the point at which calcium hydride is placed when the gaseous product is water. Water vapor reacts with the hydride to yield a stoichiometric amount of hydrogen, which is then measured. A tube 4 which is fused into the widened part of the apparatus serves as outlet. The reaction vessel is introduced into one of the channels in a block of stainless steel up to the point indicated on the diagram by the dotted line. (The tube containing the standard is placed in the other block channel to the same point). The block is in the form of a cylinder 24 x 150 mm with two channels parallel to the axis. The block, which is wrapped in asbestos paper, is then placed in a horizontal tubu-

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*Connecting the windings of the tube filaments in order to get 11-12 V is inadmissible because when this is done the two parts of the set-up are connected.

**Resistances R_3 and R_4 = 10 Ω, R_7 = 300Ω, $R_5 + R_1/2$ = 300Ω, where R_1 is the resistance of the platinum or nichrome wire (cross-section 0.1-0.2 mm) fused into buret A. The value of the variable resistance R_6 chosen depends on the sensitivity of the galvanometer K.

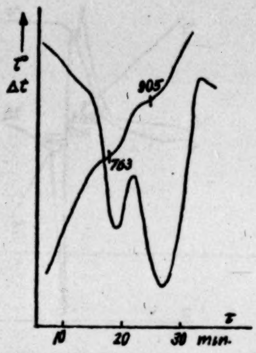

Figure 2 Thermogram for dolomite (wt 3 g)

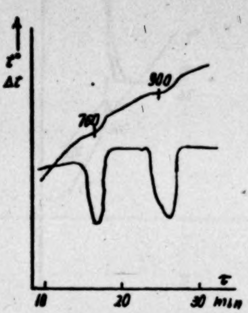

Figure 3. Thermogram for dolomite (wt. 0.15 g)

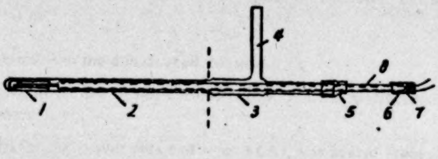

Figure 4. The reaction vessel and the method used for sealing it (schematic)

lar oven which can be controlled to give even heating (the best is a linear rate of heating). It is important that both the channels in the block are in a horizontal plane so as to ensure equal heating conditions for sample and standard.

When the test material melts during the heating the oven must be inclined so that the melt cannot flow out of the tube.

The method described above was designed for investigating processes occurring during the thermal decomposition of various substances. We shall give an example of the thermograms obtained – a record obtained for the dehydration of the septihydrate of magnesium sulfate.* Only 0.0989 g of $MgSO_4 \cdot 7H_2O$ was used. Examination of the photograms on Figure 5 clearly shows that the thermal processes which occur at temperatures below 100 are not connected with the evolution of water vapor but correspond to an incongruent melting of the hydrates. The step-like shape of the curve recorded for the volume of gas liberated indicates a step-like character for the dehydration process. It is thus possible to make quantitative calculations and to determine the composition of the intermediate hydrates. The considerable stability of the unihydrate $MgSO_4 \cdot 7H_2O$ (kieserite) as compared with the other intermediate forms is another noteworthy fact. it is stable within the range

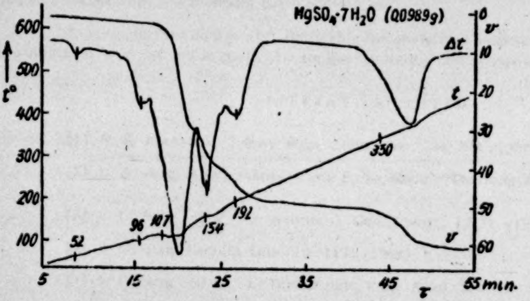

Figure 5. Thermogram of semptihydrate of magnesium sulfate. v = degree of gasification

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* N.P. Anoshina took the thermograms adduced

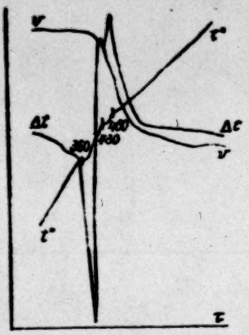

Figure 6. Thermogram of potassium chloride decomposition. v — curve of oxygen liberation.

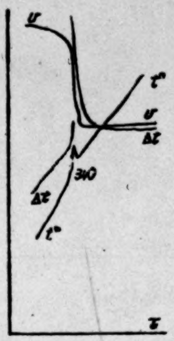

Figure 7. The same, but with manganese dioxide present.

200-350° when it is converted into the dehydrated form.

Another example of the use of this method is in a study of the thermal decomposition of certain oxygen-containing compounds.

Figure 6 illustrates the curves obtained when $KClO_3$ was heated alone while Figure 7 illustrates the curves obtained when the same material was heated with manganese dioxide as a catalyst. In the first instance the salt melted at a temperature of 360° and was accompanied by an endothermic effect, after which decomposition with evolution of oxygen set in (exothermic effects at 430 and 460°). In the second instance a rapid decomposition of the salt started at 340° – which is lower than the melting point of the salt – and evolution of gas finished rapidly.

By measuring the volume of oxygen evolved by means of the photogram it is possible to determine the amount of chlorate in a sample even without preliminary separation from other components.

SUMMARY

Examples which are given above show that the method suggested can find wide application in research laboratories for the study of various thermal processes.

It would also be very useful for studying many other processes involving the evolution of gas e.g., electrochemical and biochemical processes, etc.

Finally, this method is also applicable for analytical purposes both for carrying out ordinary gas-volumetric analysis and in particular for quantitative phase analysis.

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DETERMINATION OF CARBON AND HYDROGEN IN ORGANIC COMPOUNDS CONTAINING SULFUR AND NITROGEN, IN THE PRESENCE OF CATALYSTS

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In our first communications [1,2] we indicated that organic compounds can be analyzed rapidly and accurately by using amorphous chromic oxide obtained by the decomposition of ammonium bichromate, as a catalyst in elemental organic analysis.

It was shown that the analysis can be carried out in an atmosphere of pure oxygen when its rate of flow is increased to 350 ml/minute without decreasing the accuracy of the method.

The adsorption of oxides of nitrogen outside the combustion tube by means of oxidizing agents was verified. The apparatus was considerably simplified and the time for analysis was cut by 8-10 times.

Organic compounds containing C, H, O and N were analyzed during the course of the work indicated above.

In the present article we shall describe a method for the analysis of organic compounds which contain S and halogens in addition to C, H, O, and N.

When the oxygen rate was increased one would have expected that some of the halogens and sulfur would escape into the absorption apparatus. Our experiments showed that a layer of metallic silver 10 cm long (weight 6-7 g) completely absorbed sulfur oxides and halogens when using a 10-12 mm diameter tube at 650-750°. Lead chromate could be used instead of silver but the layer thickness had then to be increased to 20 cm.

Certain complications arise when organic compounds containing halogens are analyzed. When such compounds are analyzed the results for carbon are, as a rule, one, two, or even more percent lower than the theoretical value, according to how much halogen is present. The greater the halogen content the worse the results.

Halogens do not affect the accuracy of hydrogen determinations. It must be noted however that when fresh catalysts are used for the analysis of organic compounds containing halogens, the results are completely satisfactory. Subsequent analysis with the same catalyst gives low results for carbon. Nevertheless, since the catalyst is easily prepared and is cheap and easily available, while refilling the tube does not present any difficulties or take a long time, in individual cases where the halogen content is low it is possible to analyze the organic compound containing halogens by our method in which the catalyst is changed after each determination.

Coal, petroleum, fuel oil, oils and other technical products can be successfully analyzed using our method.

EXPERIMENTAL

The tubes were filled as follows (Fig. 1).

A small asbestos stopper was placed at a distance of 40-50 mm from the end of the tube and then a layer of metallic silver ca. 100 mm long and a 150 mm layer of granular chromic oxide kept in position by asbestos plugs. The silver was in the form of gauze, or packed narrow ribbon (1-2 mm wide) or wire, etc.

ANALYTICAL PROCEDURE

The freshly filled combustion tube was heated for 2-3 hours in a stream of oxygen.

When the tube was not in use it was sealed with a calcium chloride tube; before using, a stream of dry oxygen was passed for 10-20 minutes through the tube connected to the absorption apparatus. The apparatus was then disconnected and transferred to the balance room, where it was kept for 15-20 minutes before weighing.

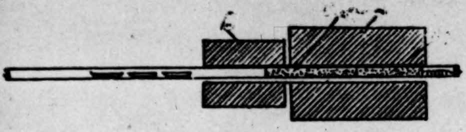

Fig. 1.

The sample, varying in weight from 0.06 to 0.30 was arranged in one or more boats according to the amount taken and the character of the substance analyzed. The contents of the tared boats were covered with calcined chromic oxide from a sealed tube.

Two electric furnaces were used for heating, the larger one A was 250-300 mm long while Б, the smaller was 150-180 mm. The temperature of the large oven was kept at 700-750° all the time.

The second small furnace served for igniting the substance and for calcining the empty tube, it should therefore heat and cool rapidly. This furnace should be movable. The small oven was fitted on after introducing the sample in the boat into the tube. When the absorption apparatus had been connected and the sample introduced the small furnace, heated up to 700-800°, was moved up. The furnace was moved up to the boat containing the substance so as to cover $^1/_3 - ^1/_2$ of the length of the boat. When this had been done the oxygen rate was increased to 150-200 ml/minute. When the substance had been ignited the furnace was moved back and, when necessary (red sooty flame) the oxygen flow increased to 250-300 ml/minute.

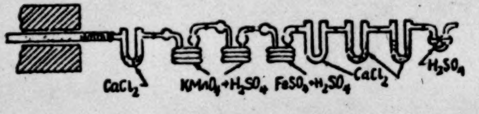

Fig. 2.

When all the substance in the first boat had been burnt, the substance in the second boat was treated likewise. The time taken for ignition was 1-3 minutes according to the amount and nature of the test substance. Finally the tube was heated for 5-10 minutes with the oxygen still running, after which analysis could be considered complete. The apparatus was disconnected, and weighed, and the percentage of carbon and hydrogen calculated.

Anhydrous calcium chloride was used for absorbing water, while ascarite or lumps of KOH were used for trapping CO_2. When compounds which contained sulfur and nitrogen in addition to carbon and hydrogen were analyzed, 1-3 traps containing an oxidizing mixture, and one trap containing a saturated solution of ferrous salt (ferrous sulfate) in 30% H_2SO_4 were placed after the water absorption train (Fig. 2).

Concentrated H_2SO_4 must be used for preparing the oxidizing mixture. Concentrated H_2SO_4 was distilled and the first one third laid aside, the other two-thirds of the distillate was collected and stored in a bottle fitted with a ground glass stopper. The 0.25% solution of $KMnO_4$ was prepared in concentrated H_2SO_4.

Examples of the results obtained for the analysis of organic compounds, coal and peat, containing sulfur and halogens are given in Tables 1 and 2.

We wish to express our thanks to the Chief of the Fuel Laboratory of the F. E. Dzerzhinsky All-Union Scientific Thermotechnical Institute, T. A. Zikeev, for his gift of a number of samples of fuel and for his continued interest in our work.

SUMMARY

1. A method is described for the quantitative determination of C and H in organic compounds containing sulfur and nitrogen.

TABLE 1

No.	Substance	Calculated in %		Found in %		Δ in %	
		C	H	C	H	C	H
1	Sulfosalicylic acid	33.09	3.95	33.04	3.99	−0.05	+0.03
		33.09	3.95	32.97	4.10	−0.12	+0.14
2	p-Toluene sulfamide	49.11	5.30	49.32	5.31	+0.21	+0.01
		49.11	5.30	49.27	5.32	+0.16	+0.02
3	Bis(1,1-dimethylpentene-3-one-sulfide)	66.13	8.72	66.26	8.57	+0.13	−0.15
		66.13	8.72	66.08	8.71	−0.05	−0.01
4	Sulfanilic acid	41.60	4.07	41.53	4.11	−0.07	+0.04
		41.60	4.07	41.67	4.17	+0.07	+0.10
5	Naphthenic acids	51.71	4.34	51.82	4.39	+0.11	+0.05
		51.71	4.34	51.79	4.43	+0.08	+0.09
6	Diphenylthiourea	68.39	5.30	68.34	5.26	−0.05	−0.04
		68.39	5.30	68.38	5.35	−0.01	+0.05
7	Thiosemicarbazide	13.18	5.53	13.36	5.46	+0.18	−0.07
		13.18	5.53	13.24	5.49	+0.06	−0.04
8	Chlorobenzene*	64.06	4.48	64.03	4.21	−0.03	−0.27
		64.06	4.48	64.15	4.38	+0.09	−0.10
9	Bromocamphor*	51.96	6.54	51.97	6.32	+0.01	−0.22
		51.96	6.54	51.71	6.76	−0.25	+0.22
10	m-Nitrochlorobenzene*	45.72	2.54	43.83	2.71	−1.89	+0.17
		45.72	2.54	42.51	2.50	−3.21	−0.04
11	p-Dichlorobenzene*	49.03	2.72	47.12	2.74	−1.91	+0.02
		49.03	2.72	46.98	2.69	−2.05	−0.04

2. It has been shown that the method is applicable to the analysis of various types of organic materials containing carbon, hydrogen, nitrogen and sulfur.

3. It has been shown that the method can be applied to the analysis of fuels.

4. By using a large combustion tube it is possible to analyze large samples by distributing the sample among more than one boat. This may prove to be very useful when the test substance contains only a very small amount of carbon and hydrogen.

5. The method has been simplified considerably, the time required for an analysis has been reduced 8-10 times without decreasing the accuracy of carbon and hydrogen determinations.

6. This gives us grounds for hoping that this method will find wide application in various research, factory, and college laboratories.

Received March 15th 1951

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* Fresh catalyst.

TABLE 2

Test No.	Fuel tested	W_t	A_d	$S^{dry}_{tot.}$	V_f	% C_t		Diff.	% H_t		Diff.	Observations
						VTI	NKI		VTI	NKI		
1	Chinese coal	0.59	–	5.51	14.71	76.16	76.04	–0.12	3.56	3.57	+0.01	Analysis checked
		0.59	–	5.51	14.71	76.16	75.81	–0.35	3.56	3.68	+0.12	in VTI(No.6466)
2.	Brown coal dust	6.56	–	1.68	39.59	52.39	52.24	–0.15	3.27	3.06	–0.21	Ditto
		6.56	–	–	39.59	52.39	52.74	+0.35	3.27	3.11	–0.16	No. 6545
3.	Coal (anthracite)	1.99	–	2.80	3.96	74.91	75.03	+0.12	1.41	1.33	–0.08	Ditto
		1.99	–	2.80	3.96	74.91	75.18	+0.27	1.41	1.38	–0.03	No. 6491
4.	Peat	11.46	–	0.38	–	45.74	46.08	+0.34	4.72	4.46	–0.26	Ditto
		11.46	–	0.38	–	45.74	45.85	+0.11	4.72	4.73	+0.01	No. 5986
5.	Intermediate product	0.70	16.08	–	20.78	72.52	72.50	–0.02	3.95	3.89	–0.06	Ditto
		0.70	16.08	–	20.78	72.52	72.58	+0.06	3.95	3.91	–0.04	No. 5834
6.	Coal "T"	0.99	22.93	2.93	8.11	68.74	68.57	–0.17	2.43	2.41	–0.02	Ditto
		0.99	22.93	2.93	8.11	68.74	68.36	–0.38	2.43	2.48	+0.05	No. 5617
7.	Coal	0.59	6.90	0.98	14.61	83.45	83.66	+0.21	4.07	4.06	–0.01	Ditto
		0.59	6.90	0.98	14.61	83.45	84.09	+0.64	4.07	4.08	+0.01	No. 5640
8.	Anthracite "ARSh"	2.83	17.25	1.93	3.88	75.28	75.49	+0.21	1.32	1.30	–0.02	Ditto
		2.83	17.25	1.93	3.88	75.28	75.23	–0.05	1.32	1.34	+0.02	No. 5644
9.	Moscow Coal	8.00	34.04	3.48	50.06	40.99	40.82	–0.17	3.24	3.16	–0.08	Ditto
		8.00	34.04	3.48	50.06	40.99	40.79	–0.20	3.24	3.15	–0.09	No. 5771
10.	Silesian Coal	5.86	18.82	2.23	38.21	59.00	59.10	+0.10	3.88	3.70	–0.18	Ditto
		5.86	18.82	2.23	38.21	59.00	59.02	+0.02	3.88	3.79	–0.09	No. 5753

Notes.

VTI – The F. E. Dzerzhnisky All-Union Scientific Research Institute.
NKI – The S. O. Makarov Nikolaev Ship-Building Institute.
W_t – moisture content of test material in %.
A_d – ash in the dry fuel in %
$S^{dry}_{tot.}$ – total sulfur in the dry mass, in %.
V_f – volatile material in the fuel, in %.
C_t – carbon in the test material, in %.
H_t – hydrogen in the test material, in %.

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THE BEHAVIOR OF CERTAIN CATIONS DURING THE COMPLEXOMETRIC DETERMINATION OF WATER HARDNESS

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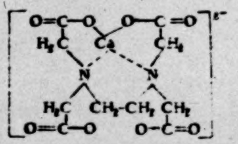
During the last six months the oleate method for the determination of water hardness has been completely superseded by a complexometric method at the Ural Electric Power Stations [1]. This method is based on the interaction between calcium and magnesium ions with the dibasic sodium salt of ethylenediaminetetracetic acid, also called Trilon B. This reaction leads to the formation of colorless inner complex compounds which are readily soluble in water.

If the ethylenediaminetetracetate ion be denoted by R^{4-}, the reaction of its bivalent salt with calcium ions (or magnesium) can be represented by the following schematic equation:

$$Ca^{2+} + Na_2H_2R = Na_2[CaR]^{2-} + 2H^+,$$

where the inner complex ion $[CaR]^{2-}$ has the structure [2]:

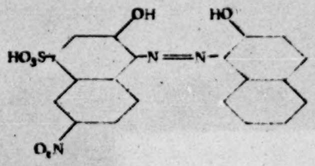


The instability constant of the complex ion is $K = \frac{c_{Ca^{2+}} \cdot c_{R^{4-}}}{c_{CaR^{2-}}} = 2.6 \cdot 10^{-11}$, while for magnesium $K = \frac{c_{Mg^{2+}} \cdot c_{R^{4-}}}{c_{MgR^{2-}}} = 2.0 \cdot 10^{-9}$.

Trilon B also gives similar soluble inner complex compounds with a number of other cations (Sr^{2+}, Ba^{2+}, Zn^{2+} etc.) [3].

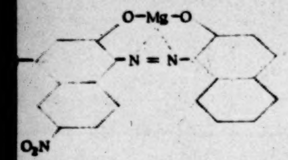
The technique of determining water hardness by complexometric methods is based on extraction of calcium and magnesium ions from their compounds with organic dyes by means of Trilon B; the dyes have different colors in the presence and in the absence respectively of calcium and magnesium ions at a definite pH value. One of the dyes recommended in the literature is Eriochrome Black T [4] which is manufactured in Russia under the trademark "Chromogen Black special ET-00 ", while we have suggested two dyes, also produced in Russia which possess functional-analytical groups similar to those of Eriochrome Black T; these are Acid Chrome Blue K and Acid Chrome Dark Blue [5,10]. Very little has been said in the literature about the reaction mechanism between the dyes indicated above and calcium and magnesium ions; there are only formal indications of the character of the color change of the dye in alkaline media upon the addition of solutions containing calcium and magnesium salts.

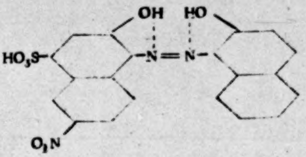
Chromogen Black, special ET-00, is a monoazo dye with a structural formula:



In alkaline media, in the presence of calcium and magnesium ions and in acid media, the dye is colored wine-red.

We postulate that in both cases we have the phenomenon of inner complex formation via the calcium and magnesium ions in alkaline media and through the hydrogen ion in acid media:



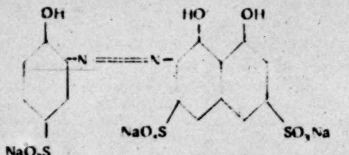


A similar mechanism can also be postulated in the case of the other two indicators mentioned above. The color of the dye in alkaline media in the presence of calcium and magnesium ions and in acid media is red in each case, while the color is violet in alkaline media not containing calcium and magnesium ions. The structural formulas of Acid Chrome Blue K (a) and Dark Blue (b) are as follows:

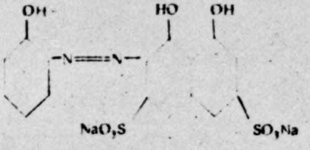
TABLE 1

Sensitivity of the Indicators to Various Cations

Cation examined and pH of the solution		Concentration of Cation Detected by the Indicator					
		Milli-equivs / liter			g/mml		
		Chromogen Black ET-00	Acid Chrome Blue K	Acid Chrome Dark Blue	Chromogen Black ET00	Acid Chrome Blue K	Acid Chrome Dark Blue
Ca^{2+}	9.8	$7\cdot10^{-4}$	$7\cdot10^{-3}$	$7\cdot10^{-3}$	$1.4\cdot10^{-8}$	$1.4\cdot10^{-7}$	$1.4\cdot10^{-7}$
Mg^{2+}	9.8	$7\cdot10^{-3}$	$1.5\cdot10^{-3}$	$1.5\cdot10^{-3}$	$8.4\cdot10^{-8}$	$2.0\cdot10^{-8}$	$2.0\cdot10^{-8}$
Zn^{2+}	9.8	$3.6\cdot10^{-3}$	$3.5\cdot10^{-3}$	$3.5\cdot10^{-3}$	$1.1\cdot10^{-7}$	$1.1\cdot10^{-7}$	$1.1\cdot10^{-7}$
Mn^{2+}	9.8	$3.5\cdot10^{-3}$	$3.5\cdot10^{-3}$	$3.5\cdot10^{-3}$	$1.1\cdot10^{-7}$	$1.0\cdot10^{-7}$	$1.0\cdot10^{-7}$
Cu^{2+}	9.8	$7\cdot10^{-3}$	$3.5\cdot10^{-3}$	$3.5\cdot10^{-3}$	$2.0\cdot10^{-7}$	$1.0\cdot10^{-7}$	$1.0\cdot10^{-7}$
Ca^{2+}	12.3	$2.8\cdot10^{-2}$	$7\cdot10^{-3}$	$7\cdot10^{-3}$	$5.6\cdot10^{-7}$	$1.4\cdot10^{-7}$	$1.4\cdot10^{-7}$
Mg^{2+}	12.3	$1.7\cdot10^{-3}$	$1.7\cdot10^{-3}$	$1.7\cdot10^{-3}$	$2.0\cdot10^{-8}$	$2.0\cdot10^{-8}$	$2.0\cdot10^{-8}$
Zn^{2+}	12.3	$3.5\cdot10^{-3}$	$3.5\cdot10^{-3}$	$3.5\cdot10^{-3}$	$1.1\cdot10^{-7}$	$1.1\cdot10^{-7}$	$1.1\cdot10^{-7}$
Mn^{2+}	12.3	$3.5\cdot10^{-3}$	$3.5\cdot10^{-3}$	$3.5\cdot10^{-3}$	$1.0\cdot10^{-7}$	$1.0\cdot10^{-7}$	$1.0\cdot10^{-7}$
Cu^{2+}	12.3	$7.0\cdot10^{-3}$	$3.5\cdot10^{-3}$	$3.5\cdot10^{-3}$	$2.2\cdot10^{-7}$	$1.1\cdot10^{-7}$	$1.1\cdot10^{-7}$

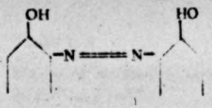


a



b

The color of the indicator in alkaline media in the presence of calcium and magnesium ions and in acid media in their absence is rose while in alkaline media in the absence of calcium and magnesium ions, the color is bluish-grey. The characteristic group in all three dyes is not specific for calcium and magnesium ions.



We experimentally determined the sensitivity of the three indicators toward calcium, magnesium, zinc, copper, and bivalent manganese (in the presence of reducing agents). The results are given in Table 1.

Table 1 shows that the three dyes are highly sensitive in alkaline media to Ca^{2+}, Mg^{2+}, Zn^{2+}, Mn^{2+}, Cu^{2+}. The sensitivity of Chromogen Black ET-00 to calcium and magnesium depends markedly on the pH of the test; it increases with increasing pH from 9.8 to 12.3.

The possibilities of determining the cations mentioned above in the presence of one of the three indicators by binding them into inner complex anions with Trilon B, depends on the ratios of the instability constants of the complex ions formed by a given cation with the indicator and with Trilon B respectively. The nature of the effect of the cations indicated, and the results for the determination of water hardness by a complexometric method, also depend on these ratios. The cations most likely to be present in the natural or processed water are Fe^{2+}, Fe^{3+}, followed by Al^{3+}, Mn^{2+}, Zn^{2+}, Cu^{2+}.

Zinc ions form (Table 1) red complexes with dyes and are quantitatively extracted from them by Trilon B, i.e., the instability constants of the inner complex ions of zinc with the dyes are greater than the instability constants of the inner complex anions formed between zinc and Trilon B.*

When water hardness is being determined, Zn will therefore be titrated with Trilon B in the same way as Ca and Mg so that the results will be higher by an amount equal to the Zn content. Zn is quantitatively determined by Trilon B in the presence of one of the indicators described (Table 2).

The behavior of Mn ions in complexometric methods of determining water hardness may be characterized as follows. After the addition of a buffer solution and indicator to a test sample containing Mn^{2+}, the red color which originally develops gradually becomes paler and the solution becomes eventually colorless. The explanation is probably as follows: in alkaline media the most stable valencies of Mn are +3 and +4 [7]. Mn^{2+} ions are easily oxidized at a pH of 9-12 by oxygen dissolved in the water, and difficultly soluble hydroxides of tri and quadrivalent manganese which adsorb the dye are formed.

The addition of a reducing agent such as a solution of hydroxylamine hydrochloride to the test sample allows the manganese to remain in the test solution as Mn^{2+} ions which give red complexes with the indicator. Trilon B extracts Mn^{2+} quantitatively from these complexes which means that the instability constant of the inner complex ions of Mn^{2+} with the indicator is greater than the instability constant of the complex ion formed between Mn^{2+} and Trilon B.** Mn^{2+} is quantitatively determined on titration with Trilon B in the presence of the indicators enumerated above, consequently it interferes during the determination of water hardness by complexometric methods and leads to high results.

TABLE 2

Results of the Determination of Zinc with Trilon B

Conc. of Zn^{2+} in test material in mg/l	Zn^{2+} found mg/l
11.7	11.65
7.02	7.02
5.85	5.9
3.51	3.49
1.17	1.15
0.58	0.58

Cu^{2+} ions also (Table 1) form red complexes with dyes. A test solution containing Cu^{2+}, a buffer, and dye remains red even when Trilon B is added. If the reagents are added together in the reverse order, i.e., if the dye is added to the test solution containing Cu^{2+} ions, Trilon B, and a buffer, then the test solution remains blue. The only possible explanation for this is that the values of the instability constants of the complexes formed between Cu^{2+} ions and the indicator and Trilon B*** respectively are similar.

Cu^{2+} will accordingly not titrate with Trilon B but the determination of water hardness in the presence of Cu^{2+} is impossible because there is no transition point for the indicator.

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* The instability constant of the complex zinc-Trilon B is 7.1 · 10^{-1} [9].

** The instability constant of the complex ion formed between Trilon B and Mn^{2+} is 3.4 · 10^{-14} [9].

*** The instability constant of the complex ion formed between Trilon B and Cu^{2+} is 4.1 · 10^{-19} [9].

TABLE 3

Results of Determination of Mn^{2+} with Trilon B in Presence of Hydroxylamine Hydrochloride

Conc. of Mn^{2+} in test material in mg/l	Mn^{2+} found, mg/l
0.1	0.15
0.2	0.21
0.4	0.43
0.6	0.65
0.8	0.82
1.0	1.04

TABLE 4

Results of the Determination of Total Hardness in the Presence of Zn^{2+} and Cu^{2+}

Water hardness in degrees	Amount present in, mg/l		Amount of 10% solution of Na_2S added	Hardness determined, in degrees
	Cu^{2+}	Zn^{2+}		
10	0.5		–	Transition point absent
10	0.5		1	10
1	0.5		1	1
0.2	0.5		1	0.2
0.05	0.5		1	0.05
10	–	7	–	11.1
10		7	1	10.0
0.2		5	1	0.2
0.05		1	1	0.05

Al^{3+} ions at concentrations up to 20 mg/liter do not affect hardness determinations. Fe^{2+} ions on addition of a buffer solution, i.e., in alkaline media are rapidly oxidized by dissolved oxygen to Fe^{3+}, so that it is always Fe^{3+} ions which have to be dealt with during water hardness estimations by complexometric methods. Water hardness can be determined in the presence of up to 10 mg/liter iron. The end point can be clearly detected though the brown color of the ferric hydroxide distorts the blue color of the dye.

Interference from Fe^{3+} and Al^{3+} can be eliminated by diluting the test solution with distilled water till the concentration is below 10 mg/liter for Fe^{3+} and less than 20 mg/liter for Al^{3+}.

This method is no good for Cu^{2+}, Zn^{2+} and Mn^{2+}, because they interfere at very low concentrations. Interference on the part of these elements can be eliminated by combining them into stable complexes or precipitating them in the form of difficultly soluble compounds.

The most insoluble compounds of copper and zinc are the sulfides whose solubility products are $8.5 \cdot 10^{-45}$ and $7.9 \cdot 10^{-25}$, respectively [6].

Since the solubility of these sulfides is very low Trilon B will not extract Cu^{2+} and Zn^{2+} from them, so that water hardness can be determined with Trilon B in the presence of the sulfide precipitates without any preliminary filtration of the sulfides. We are of course dealing with interference from low concentrations of Zn^{2+} and Cu^{2+} when determining water hardness, so that any sulfides formed are either colloidally dispersed or form only a small amount of precipitate.

In such a case the addition of 1 ml of 5-10% sodium sulfide to the test solution before addition of the buffers and the indicator completely eliminates interference from Cu^{2+} and Zn^{2+} (Table 4).

Interference from Mn^{2+} can be eliminated by addition of hydroxylamine hydrochloride. In this case titration is normal but the hardness will be the sum of Mn^{2+}, Ca^{2+} and Mg^{2+}.

The amount of Mn^{2+} in natural water does not exceed 0.5 mg/l [9] so that its presence will have practically no effect on the results.

SUMMARY

1. The behavior of Ca, Mg, Zn, Mn, Cu, Al, Fe during the complexometric determination of water hardness with Trilon B in the presence of the indicators — Chromogen Blue ET-00, Acid Chrome Blue, and Acid Chrome Dark Blue, has been considered.

2. Methods for eliminating interference from the various cations have been indicated.

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* See Consultation Bureau Translation page 1841.

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MICROCRYSTALLOSCOPIC REACTIONS FOR CYANIDES

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The reaction based on formation of a precipitate of silver cyanide is the best of the characteristic and sensitive microcrystalloscopic reactions for cyanides. The amorphous precipitate which is initially formed is recrystallized from concentrated nitric acid or is treated with ammonia until it dissolves; according to the amount of ammonia which evaporates fine crystals of silver cyanide fall out. When this reaction is carried out in a gas cell fine crystals of silver cyanide are formed. Coarse crystals of silver cyanide are obtained when precipitation is carried out from more concentrated solutions of cyanides, in such cases the cyanide anion content should not be less than 5μg [1].

Organic reagents of high sensitivity and specificity [2], are widely used in qualitative and quantitative analyses. Benzidine in the presence of cupric acetate which forms a blue crystalline precipitate of the oxidation products of benzidine with cyanide solution is one of the organic reagents used for microreactions for cyanides. Similar precipitates are given by tolidine, dianisidine and hydrocerulignone [3]. These reactions are not specific, since they also form crystalline precipitates in the presence of oxidizing agents ($Cr_2O_7^{2-}$, MnO_4^- etc.). Recently metal-organic compounds have started coming into use as reagents (triphenyltin chloride, mercury succinimide, and benzidine etc). [4].

During a study of the analytical properties of certain mercuriated aromatic amino compounds we established that they could be used as analytical reagents for anions. These compounds form characteristic crystalline precipitates with various anions and by a study of crystal form and certain other crystallooptical constants the presence or absence of certain anions can be determined. The reactions which occur between mercury organic compounds and the anions proceed as follows

$$RHgAc + X^- \rightarrow RHgX + Ac^-,$$

where X^- is the anion to be detected while Ac^- is the acetate anion. By means of the crystalline precipitates formed by interaction with these mercury organic compounds (2), microgram quantities and fractions of a microgram of the test anion can be detected in a drop of solution. The present article is the result of our studies on microcrystalloscopic reactions between certain mercury organic compounds and cyanides. 20 mercury organic compounds prepared by mercuriating aromatic amino compounds by methods indicated in the literature [5], were tested.

Of the compounds tested by us the following gave crystalline precipitates with cyanides.

1, 4 - aminophenylmercuryacetate $NH_2C_6H_4HgAc$.
1, 4 - ethylaminophenylmercuryacetate $(C_2H_5)NH{\cdot}C_6H_4HgAc$.
1, 4 - dimethylaminophenylmercuryacetate $(CH_3)_2N{\cdot}C_6H_4HgAc$;
1, 4 - ethylbenzylaminophenylmercuryacetate $(C_2H_5)(C_6H_5CH_2)N{\cdot}C_6H_4HgAc$.
1, 4 - diethylaminophenylmercuryacetate $(C_2H_5)_2N{\cdot}C_6H_4HgAc$.
3 - methyl - 4, 1 - aminophenylmercuryacetate $CH_3(NH_2)C_6H_3HgAc$.
3 - nitro - 1, 4-aminophenylmercuryacetate $NO_2(NH_2)C_6H_3HgAc$.
1, 2 - toluidine - 4, 6 - dimercuryacetate $CH_3(NH_2)C_6H_2(HgAc)_2$.

The experimental procedure was as follows: a drop of the test cyanide solution was placed on an object glass together with a drop of freshly prepared saturated solution of the mercury organic compound in water or in 5-10% acetic acid, and the formation of a crystalline precipitate observed under the microscope. The compounds listed with the exception of 1, 2 - toluidine - 4, 6 - dimercuryacetate form crystalline precipitates also with Cl^-, Br^-, I^-, CNS^- and with some other anions, so that in the presence of these anions the reactions for cyanide are not specific. In order to increase the specificity, the reactions were carried out in a gas cell. However, even under these conditions some of the reagents listed were still inapplicable. Thus, 1, 4 - dimethylaminophenylmercuryacetate gave a comparatively highly sensitive reaction for cyanides in solution (0.1 g CN) but did not give a crystalline precipitate in the gas cell, while 3 - nitro - 1, 4 - aminophenylmercuryacetate though capable of forming a crystalline precipitate in the gas cell can only detect CN if the latter is present in amounts of not less than 1 μg CN^-.

Three compounds, viz. 1, 4 - ethylbenzylaminophenylmercuryacetate, 1,4 - dimethylaminophenylmercuryacetate, and 1, 2 - toluidine - 4,6 - dimercuryacetate form crystalline compounds both with dilute solutions of cyanides and with small amounts of cyanides in a gas cell, and can therefore be used for the specific detection of CN^-.

The table below includes some of the results characterizing the crystalline precipitates which are formed by the interaction of cyanide solutions (without the use of a gas cell) with these three compounds.

TABLE

Reagent	1,4-ethylbenzylaminophenylmercuryacetate $(C_2H_5)(C_6H_5CH_2)N{\cdot}C_6H_4HgAc$	1,4-dimethylaminophenylmercuryacetate $(CH_3)_2N{\cdot}C_6H_4HgAc$	1,2 toluidine-4,6-dimercuryacetate $CH_3(NH_2)C_6H_2(HgAc)_2$
Composition of precipitate	$(C_2H_5)(C_6H_5CH_2)N{\cdot}C_6H_4HgCN$	$(CH_3)_2N{\cdot}C_6H_4HgCN$	$CH_3(NH_2)C_6H_2(HgCN)_2$
Crystal form	Plate, rosettes	Plates, rosettes, rods	rosettes in the form of snow flakes
Limit of identification in μg	0.25	0.25	0.25
Maximum crystal size in μ	140	90	120
Pleochroism	Intense, yellow, red, green	Intense, yellow, red, green	Weak yellow, blue
Extinction angle of crystal	5-7	35-37°	90°

When the reactions are carried out in a gas cell the sensitivity increases and excess of other ions do not interfere appreciably. Only S^{2-} seems to have a strong effect. If the amount of S^{2-} exceeds that of the CN^- ions in the test solution, then the reaction must be modified somewhat. To a drop of the test solution on the bottom of a gas cell, a drop of a 10-15% solution of lead acetate was added the effect of the S^{2-} was thus eliminated, and the solution was then mixed with a drop of 10% acetic acid. The cell was sealed with a cover glass, on the lower surface of which a small drop of reagent solution had been placed, after which the cell was mounted on the miscroscope object stage. The formation of precipitate crystals was observed in the upper drop using a small stop. The time which the reaction took did not exceed 10 minutes.

An acetic acid solution of 1, 4 -ethylbenzylaminophenylmercuryacetate forms a crystalline precipitate consisting of colorless or pale yellow rosettes and plates of up to 240 μ in size (Figure 1) with cyanides in a gas cell.* The limit of identification is 0.25 μg CN^- while the limiting concentration is 1:8,000. Limiting ratios (at 0.25μgCN^-) are :

$CN^-:Cl^-$ (or Br^-) = 1:80;
$CN^-:Fe(CN)_6^{4-}$ (or $Fe(CN)_6^{3-}$) = 1:65;
$CN^-:CNS^-$ (or I^-) = 1:40;
$CN^-:S^{2-}$ (or SO_3^{2-}) = 1:35;
$CN^-:NO_2^-$ = 1:10.

The reagent crystals which are precipitated at the edges of the drop of reagent solution differ appreciably from crystals of the cyanide precipitate. The reagent crystals form colorless parallelograms which exhibit intense pleochroism: the angle of extinction is 35-37°, while the acute angle of the parallelogram is 70°. (Figure 2). It is essential to note that the drop dries out very slowly in the gas cell and the appearance of reagent crystals can only be observed on removal of the drop from the cell.

1,4 Dimethylaminophenylmercuryacetate in aqueous or acetic acid solution reacts with cyanides in the gas cell to form colorless crystalline precipitates consisting of plates, rods, and rosettes, with sizes up to 55μ in aqueous solution (Figure 3) and up to 500μ in acetic acid solution (Figure 4). The limit of identification in aqueous solution is 0.03μg CN^- while the limiting concentration is 1:65,000. The

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* All the photographs were taken at a magnification of 100, Figure 3 at a magnification of 450. (See Plate, page 213.)

Limit of Identification in acetic acid solution is 0.25 μg and the Limiting Concentration 1:8,000. The limiting ratios with other anions are the same as for reactions with 1,4-ethylbenzylaminophenylmercuryacetate, with the exception of reactions in the presence of NO_2^- ions. The presence of a 35-fold excess of NO_2 as compared with CN^- does not interfere with detection of CN. The reagent separates out in the form of bunches of fine colorless needles on drying out along the drop edges (Figure 5). The pleochroism of the reagent crystals is very weak: yellow, red, and green; the extinction angle of the crystals is 16-19°.

1,2-toluidine-4,6-dimercuryacetate is a highly sensitive and specific reagent for cyanides, since in aqueous solution it does not form crystalline precipitates with any other anions except CN^-. This reagent can consequently be used for the detection of cyanides in solutions containing excess of other anions, and can be used with even greater success for the detection of cyanides in a gas cell. The precipitate crystals consist of colorless rosettes like snow-flakes with sizes up to 120μ (Figure 6). The Limit of identification for reactions carried out in a gas cell is 0.03μg CN^- while the Limiting Concentration is 1:65,000. $S^=$ interferes with the detection of CN^- in solution. In such cases a drop of 10-15% lead acetate should be added to 3-4 drops of test solution. The solution is then centrifuged when it is ready for testing for CN^-. The limiting ratios when a gas cell is not used (for 0.25 μg of CN^-) are as follows:

$CN^-:Cl^-$ (or Br^-, I^-, SO_4^{2-}) = 1:50;
$CN^-:CNS^-$ (or NO_2^-) = 1:25;
$CN^-:FE(CN)_6^{3-}$ (or $Fe(CN)_6^{4-}$, $Fe(CN)_5NO^{2-}$) = 1:20;
$CN^-:S^{2-}$ = 1:3.

The limiting ratios for reactions carried out in a gas cell (for 0.03μgCN^-) $CN^-:Cl^-$ (or Br^-, I^-, CNS^-, $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$, $Fe(CN)_5NO^{2-}$, S^{2-}) with addition of lead acetate = 1:50, $CN^-:NO_2^-$ (or SO_4^{2-}) = 1:25, $CN^-:S^{2-}$ without addition of lead acetate = 1:5. The reagent crystallizes out along the edges of reagent drops in the form of fine colorless rods and needles (Figure 7).

We tested 1,2-toluidine-4,6-dimercuryacetate for the detection of cyanides in air and in certain organs of animals which had died from KCN poisoning.

If a drop of this reagent is placed on the inner wall of a gas cell, containing 50 ml air with 1.2μg CN^-, crystals of the cyanide can be detected in the drop after 10 minutes. Under similar conditions CN^- was detected in a liter of smoke from a certain type of tobacco and also when tests were made out under production conditions of galvanized baths containing KCN. By means of a gas cell technique we determined CN^- in the liver and heart of a white rat poisoned with 2.5 mg KCN.

SUMMARY

1. Three microcrystalloscopic reactions are proposed for the detection of CN^- ions which are based on the formation of crystalline precipitates when 1,4-ethylbenzylaminophenylmercuryacetate, 1,4-dimethylaminophenylmercuryacetate and 1,2-toluidine-4,6-dimercuryacetate respectively react with cyanides. Some crystallooptical constants are given for the crystals formed. The Limit of Identification is 0.03 μgCN^-. It only takes 5-10 minutes to carry out a test.

2. 1,2-toluidine-4,6-dimercuryacetate is used for the detection of cyanides in solution. The Limit of Identification is 0.25μg CN^-. With the exception of S^{2-}, interference from which can easily be eliminated by the addition of lead acetate, excess of Cl^-, Br^-, I^-, CNS^-, NO_2^-, SO_4^{2-} do not appreciably affect the results.

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THE ANALYTICAL USE OF POTASSIUM MANGANATE HYDROLYSIS

S. F. Zavgorodny

Quantitative determination of manganate and permanganate when they occur simultaneously is based on the oxidation-reduction process

$$3MnO_4^{2-} + 2H_2O \rightarrow MnO_2 + 4OH^- + 2MnO_4^- , \qquad (1)$$

which is sometimes called the manganate hydrolysis. Walde and Schuh [1] first proposed that this reaction could be used for analytical purposes. For this end the test solution is treated with CO_2 until MnO_2 ceases to be formed, when it is dissolved in sulfurous acid ($SO_2 + H_2O$) and the Mn^{2+} determined by the pyrophosphate method.

It has been postulated that the reaction proceeds as follows -

$$3K_2MnO_4 + 2CO_2 = 2K_2CO_3 + MnO_2 + 2KMnO_4. \qquad (2)$$

Total manganate and permanganate are first determined in another aliquot by the oxalate method. Sokolova [2] decomposed the manganate with potassium bisulfate

$$3K_2MnO_4 + 4KHSO_4 = 2KMnO_4 + MnO_2 + 4K_2SO_4 + 2H_2O. \qquad (3)$$

When the MnO_2 has been filtered off the permanganate in solution is then also determined by the oxalate method. According to Centnerszwer [3] who checked the CO_2 method, reaction (2) only proceeds when there is five times more permanganage than manganate, if there is no excess the error in determination can be as much as 50 %. This author concluded that in the absence of permanganate or when only a small amount of it is present in solution, the decomposition of manganate by CO_2, or by acids is accompanied by formation of oxide and not dioxide of manganese.

$$6K_2MnO_4 + 4CO_2 = 4KMnO_4 + 4K_2CO_3 + Mn_2O_3 + O. \qquad (4)$$

Centnerszwer proposed that the manganese be decomposed with H_2SO_4 or HNO_3 (10-15%) and depending on the permanganate content of the solution, calculate the analytical results according to (2) or (4). The necessity of using two equations for calculating the results is a real drawback of the method. Moreover the use of comparatively concentrated solutions 0.2 M $KMnO_4$ and 0.5 M $H_2C_2O_4$ - must also lead to an additional error which is considerable.

In order to find out what are the optimum conditions for the analytical application of the manganate hydrolysis [1] the author of the present article experimentally verified the CO_2, bisulfate, and HNO_3 - H_2SO_4 method. The manganate used for analysis was prepared by boiling 0.2 M $KMnO_4$ with 50% KOH. The test mixtures were prepared before each determination by pouring into a 250 ml standard flask measured amounts of K_2MnO_4 and $KMnO_4$ solutions respectively and the solutions made up to standard volume with a 2-3 N KOH. The original solutions contained 0.00547 g K_2MnO_4 and 0.04914 g $KMnO_4$.

The procedure adopted was as follows. 50 ml of the manganate-permanganate mixture was treated with the respective reagent to decompose the manganate. The solution was then filtered free from MnO_2 by means of a No. 3 sintered glass filter, the precipitate was washed free of permanganate with warm water and dissolved in 0.1 N $H_2C_2O_4$ containing H_2SO_4 by warming. Excess oxalic acid was determined by means of permanganate. The filtrate containing the permanganate in solution ("both the original permanganate-'primary', - and that formed during the reaction -'secondary'") was transferred to a 250 ml standard flask and made up to the mark with water. This permanganate was also determined by the oxalate method using 50 ml aliquots. The analytical results were calculated as follows. From 1 it follows that the 12 oxygen equivalents of 3 mols of manganate correspond to the 2 oxygen equivalents of the 2 mols of MnO_2. Consequently, by multiplying the number of mols of $H_2C_2O_4$ (0.1 N) used for the determination of MnO_2 by 6, and the titer for 0.1 N K_2MnO_4 by 0.004928 we can find the amount of manganate in the aliquot taken. In order to determine the amount of permanganate formed during the reaction, the value found for the manganate content is divided by 1.871. This coefficient is determined from the ratio

$$\frac{3K_2MnO_4}{2KMnO_4} = \frac{3\cdot 197.13}{2\cdot 158.03} = 1.871$$

The permanganate originally in solution before reaction is determined by subtracting the amount of permanganate formed during the reaction from the total amount of permanganate contained in the filtrate. From the results obtained, which are given in Table 1, it is clear that satisfactory results are obtained only when the solution contains not less than 10 mols of permanganate/mol of manganate and not 5 times as Centnerszwer indicated.

TABLE 1

No.	Amount taken		Molar ratio	Amount found				Method used
	K_2MnO_4, in g	$KMnO_4$, in g	$\frac{KMnO_4}{K_2MnO_4}$	K_2MnO_4 in g	K_2MnO_4 % error	$KMnO_4$ in g	$KMnO_4$ % error	
1	0.0492	0.1368	3.45	0.0377	23.40	0.1270	7.15	CO_2
2	0.0492	0.1999	5.07	0.0457	7.15	0.1964	1.73	CO_2
3	0.0492	0.3684	9.34	0.0483	1.75	0.3654	0.81	CO_2
4	0.0492	0.4402	11.15	0.0489	0.53	0.4385	0.38	CO_2
5	0.0428	0.1082	3.16	0.0328	23.18	0.0993	8.24	bisulfate
6	0.0428	0.2576	7.46	0.0412	3.69	0.2487	3.43	bisulfate
7	0.0428	0.3284	9.60	0.0423	1.02	0.3231	1.61	bisulfate
8	0.0428	0.4402	12.84	0.0425	0.42	0.4364	0.87	bisulfate
9	0.0369	0.1190	4.01	0.0343	7.06	0.1119	5.92	$HNO_3+H_2SO_4$
10	0.0369	0.1694	5.73	0.0354	4.12	0.1623	4.08	$HNO_3+H_2SO_4$
11	0.0369	0.2240	7.58	0.0359	2.71	0.2198	1.88	$HNO_3+H_2SO_4$
12	0.0369	0.2971	10.01	0.0367	0.43	0.2961	0.34	$HNO_3+H_2SO_4$

The use of only equation (4) for calculation of the analytical results did not give satisfactory results; the mean error amounted to 10-15%. By analysis of solutions of manganate not containing permanganate it was shown that in this case the amount of $KMnO_4$ and MnO_2 formed agreed with the values calculated theoretically from equation(1). Thus, when 0.1924 g K_2MnO_4 (40 ml) was decomposed with H_2SO_4, 0.0284 g MnO_2 and 0.1037 g $KMnO_4$ were obtained the theoretical values were 0.0286 and 0.1041 g, respectively

These experiments showed that Centnerszwer was wrong about the above mentioned scheme. Apparently, the source of error, during analysis of solutions where the molar ratio of permanganate to manganate is less than 10, is the formation of precipitates, the compositions of which vary between Mn_3O_4 and MnO_2. Mendeleev [4] cited the action of Na_2SO_3 on permanganate, forming a colloidal precipitate $Mn_2O_3\cdot 4(MnO_2\cdot H_2O)$ Dubois [5] indicates that a series of oxides containing MnO_2 as one of the components can exist in the range Mn_2O_3 and MnO_2. Thus, $MnO_{1.93} = Mn_{16}O_{31} = 15MnO_2\cdot MnO$ can occur. MnO_2 present in a colloidal form might also affect the accuracy of the determination of $KMnO_4$, because it adsorbs manganate in preference to permanganate. If the existence of the higher oxides indicated above is accepted as being probable, then the preferential adsorption of K_2MnO_4 can be explained in accordance with the Fajans-Hahn rule, by the formation of insoluble manganese manganate.

When there is a considerable excess of $KMnO_4$, apparently the relative amount of K_2MnO_4 adsorbed by the precipitate decreases. In order to confirm the relation obtained above, a method of additions was adopted in which a known amount of permanganate solution of known strength* was added before carrying out the decomposition of $KMnO_4$. The amount of permanganate to be added was determined from the color of the test solution. Requisite amounts of permanganate, indicated in Table 2, were added to solutions of the same concentrations as given in Table 1, in which the molar ratio of permanganate to manganate was less than 10. The results obtained were completely satisfactory.

Thus, by adding the necessary amount of permanganate to the test solution, it is possible to analyze solutions containing any ratio of the components. An analysis takes half an hour.

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* This was also successfully applied in the ferrocyanide method of analyzing solutions of manganates and permanganates when both were present simultaneously. [6]

TABLE 2

No.	$KMnO_4$ added in g	New ratio (molar) $\frac{KMnO_4}{K_2MnO_4}$	Found				Method used
			K_2MnO_4 in g	% error	$KMnO_4$ in g	% error	
1	0.3322	11.88	0.0490	−0.44	0.1363	−0.41	CO_2
2	0.3322	13.50	0.0494	+0.36	0.1994	−0.24	CO_2
3	0.3422	13.95	0.0429	−0.40	0.1079	−0.29	bisulfate
4	0.4224	19.80	0.0427	−0.27	0.2582	+0.24	bisulfate
5	0.3084	14.44	0.0368	−0.27	0.1192	+0.22	$HNO_3 + H_2SO_4$
6	0.3282	16.45	0.0370	+0.32	0.1689	−0.30	$HNO_3 + H_2SO_4$

SUMMARY

1. Methods for the analysis of manganate-permanganate solutions which are based on hydrolysis of the manganate have been checked and the limits of their application indicated. The correctness of the generally accepted scheme for manganate hydrolysis was confirmed.

2. It is postulated that the error in the determination of manganate in cases where there is a relatively low concentration of permanganate can be explained by formation of oxides intermediate between Mn_2O_3 and MnO_2, and partial adsorption of manganate by colloidal MnO_2.

3. It has been shown that preliminary addition of known amounts of permanganate to test solutions enables solutions containing any ratio of the components to be analyzed fairly accurately.

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A COMPARATIVE EVALUATION OF QUALITATIVE REACTIONS FOR BISMUTH CARRIED OUT BY TRITURATION

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As Flavitsky [1,2], and, in recent years, a number of Soviet research workers [3-9], have shown, qualitative chemical analysis involving the use of trituration methods enable the majority of elements of practical importance to be determined in their salts, minerals, and certain ores. The speed with which the method can be carried out and the extreme simplicity of the apparatus make these methods ideal ones for geological parties under field conditions [5,9]. This method, however, has not been tested very much on ores of various types, and the sensitivity and specificity of the individual reactions have not been established as clearly as they should have. Thus, Isakov [3,5] gives four examples of qualitative reactions for bismuth in which various reagents were used [ammonium thiocyante, pyrogallol, sodium thiosulfate, and ammonium hexathiocyanate chromite $(NH_4)_3 Cr(CNS)_6$] without any comparative evaluation of the different reactions.

Reactions with sodium thiosulfate are not specific for bismuth. Thus, silver, which is often present in lead ores in addition to bismuth, gives a similar color. The reaction of bismuth with ammonium thiocyante is not specific in the presence of iron because of the necessity of reducing trivalent iron with thiosulfate. The fact that these individual questions have not been dealt with fully enough hinders the wide use of the method and its adoption for field testing.

The aim of the present paper is to check the application of qualitative reagents for bismuth which are carried out by trituration on samples of galenite and other ores of a definite type, and to work out the conditions for which the reaction will be most sensitive and selective.

The ore tested was a typical polymetallic ore and in addition to bismuth contained lead, zinc, copper, antimony, arsenic, sulfur, manganese, silver, magnesium, iron, aluminum and other elements. Some samples contained considerable amounts of iron.

In all the tests bismuth was determined colorimetrically using thiourea, while in the samples of galenite containing bismuth it was determined spectrographically.

Preliminary experiments showed that H_2SO_4 does not ensure complete decomposition of the material with the formation of white colored salts. Decomposition of galenite by H_2SO_4 was particularly unsatisfactory, even after two treatments it remained undecomposed and had a grey color. The test materials were accordingly decomposed by successive treatment with HNO_3 and H_2SO_4.

Table 1 shows the advantages of treating galenite with the two acids. The sensitivity of the bismuth determination is increased. In the presence of bismuth, the color of the reaction product after trituration with $Na_2S_2O_3$, which depends on the bismuth content, varies from blood-red or brown to a weak yellow or lemon.

Four qualitative reactions for bismuth were experimentally tested with: pyrogallol, ammonium thiocyante, sodium thiosulfate and ammonium hexathiocyanatochromite.

a) Reactions with Pyrogallol

0.03 g galenite was treated in a porcelain beaker with the acids and after evaporation to dryness the residue was triturated with 3-4 crystals of pyrogallol. According to Isakov the reaction products should be colored pale green. In the test samples of galenite and the other ores the color of the reaction products varied from a pale violet to a dark violet and only on wetting with water did the change to green occur and that only in some instances. In the majority of cases, wetting the product with water led to blackening.

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* V. L. Alpatova participated in the experimental work.

TABLE 1

Bismuth content of the test samples		Color of the reaction product with $Na_2S_2O_3$ after decomposition of galenite	
in fraction of a %	in %	with H_2SO_4	with HNO_3 and H_2SO_4
units	3.2; 1.24; 1.21	from blood-red to dirty-grey	from brown to blood-red
tenths	0.86	weak red	blood-red of lesser intensity
hundredths	0.07	bismuth not detected	pale-lemon

Reactions with pyrogallol are therefore unsuitable for qualitative determinations of bismuth in galenite and in the other types of ore tested.

b) Reactions with Ammonium Thiocyanate

In the presence of trivalent iron the mixtures were colored reddish-brown. Isakov recommended that during triturations a small amount of crystalline $Na_2S_2O_3 \cdot 3H_2O$ be added to the ammonium thiocyanate in order to reduce the trivalent iron, when this was done the reddish-brown color disappears while the yellow color of ammonium thiocyanate appears. Since thiosulfate acts as a reagent for silver we used another reducing agent for iron — Na_2SO_3 – which does not give a color with bismuth, silver, or the other elements.

TABLE 2

Bismuth content of the test samples			Color after trituration with		
in fractions of a %	in %	in µg	NH_4CNS	$Na_2S_2O_3$	$(NH_4)_3[Cr(CNS)_6]$
units	in galenite 3.2;1.24, 1.12	960,373,336	intense orange	blood-red	orange-red, sometimes with grey shades.
tenths	in galenite 0.86	258	orange	from blood-red, less intense to grey-yellow	from orange-red, less intense, to light-green shades.
hundredths	in galenite 0.011, 0.071	3.3; 21	weak orange to canary-yellow	light lemon sometimes with dirty-grey shades	weak orange-red, sometimes with violet and green shades.
	in ore 0.014,0.038	4.2; 11.4			
thousandths	in the ore 0.005 0.008 0.008	1.5, 2.4;1.4	yellow	grey-yellow sometimes with greenish shades.	weak orange-red, less intense.

Reactions with ammonium thiocyanate in the presence of sodium sulfite are characterized by fair sensitivity and specificity (Table 2). By this method 0.00136 mg or 1.37 µg can be detected in 0.03 g of test material.

c) Reactions with Sodium Thiosulfate

The test powder of mineral or ore after treatment with HNO_3 and H_2SO_4 and evaporation was triturated with 1-2 crystals of sodium thiosulfate $Na_2S_2O_3 \cdot 3H_2O$. No appreciable color was observable immediately after doing this, but gradually, on standing in the air, a pale yellow color appeared which quickly changed into a stable blood-red color. Table 2 shows that these reactions with sodium thiosulfate are not so sensitive as the reactions with ammonium thiocyanate.

Using this reaction 0.00274 mg or 2.74 µg of bismuth can be detected in a sample.

d) Reactions with Ammonium Hexathiocyanatochromite

The powdered mineral or ore after treatment with the acids was triturated with 1-2 crystals of ammonium hexathiocyanatochromite. In the presence of bismuth a red-orange color develops because of the formation of $Bi[Cr(CNS)_6]$

$$Bi_2(SO_4)_3 + 2(NH_4)_3[Cr(CNS)_6] = 2Bi[Cr(CNS)_6] + 3(NH_4)_2SO_4.$$

On checking this it was observed that the red-orange color can be masked by shades of different colors from violet to green. Because this change from one color to another is not very clear cut, the reaction is less sensitive than the reactions with ammonium thiocyanate and sodium thiosulfate.

A comparison of the results obtained by the last three methods is given in Table 2.

The reaction with ammonium thiocyanate can be used as a semiquantitative method for the detection of bismuth in polymetallic ores and products obtained by treatment of these ores, since the color intensity (from orange to yellow) depends on the bismuth content of the aliquots, and is not masked by other colors.

SUMMARY

1. Comparative tests have been made of qualitative reactions for bismuth using a trituration technique with pyrogallol, ammonium thiocyanate, sodium thiosulfate, and ammonium hexathiocyanatochromite.

2. It has been established that the most sensitive reaction for bismuth is the one with ammonium thiocyanate; the intensity of the yellow color produced is dependent on the bismuth content.

3. It is better to use sodium sulfite and not sodium thiosulfate (as recommended by Isakov) for the reduction of trivalent iron when using ammonium thiocyanate for the detection of bismuth.

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DETERMINATION OF VAPORS OF FLUOORGANIC COMPOUNDS IN AIR

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Analysis of small amounts of highly volatile and gaseous fluoorganic compounds presents considerable difficulty.

The special characteristics of fluoorganic compounds necessitate special techniques for their analysis, and several of the conventional methods used for analysis of other halo-organic compounds are not applicable.

Thus, determinations by means of the lamp method which we have used for the analysis of a number of halogen compounds are out of the question, because the surface of the lamp glass is attacked by HF formed during combustion. Decomposition of fluoorganic compounds by alkali metals is impracticable because of the effect of the salts formed on neutralization on the subsequent determination of the fluorine ion. The normal method of thermal decomposition in a calcined porcelain tube is also excluded because HF reacts with the inner walls of the tube.

Analysis of micro-amounts of fluoorganic compounds is complicated further by the absence of sufficiently sensitive methods for determination of fluorine ions.

The most expedient method for determination of small amounts of elements by chemical means is the colorimetric method. Fluorine ions, however, do not give colored compounds, and the usual colorimetric method for fluorine is based on measuring the degree by which the color of various metal complexes is weakened on interaction with fluorine [1-9]. Naturally, methods based on this principle are not adequately accurate or sensitive, since measurements of the small extent of weakening of a color on an intensely colored background are extremely difficult.

Further, the known reactions of fluorine with colored complexes are themselves extremely variable with respect to pH and to the salt composition of the test solution.

All these drawbacks led us to seek for new methods of analyzing low concentrations of fluoorganic vapors.

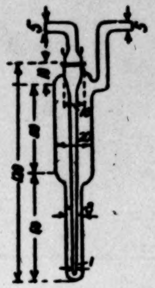
During our investigations, which were directed at working out a sensitive and accurate method, we settled on the principle of combustion of the vapors in a quartz tube with subsequent determination of the SiF_4 formed. In using this technique, it seemed interesting, for the reasons adduced above, to estimate SiF_4 by its silicon and not its fluorine content. Such an approach was justified because we already had an accurate method for determination of silicon, and preliminary results on the possible diffusion of "volatile silicon" from the heated quartz tube were favorable.

After testing some volatile fluoorganic compounds we became convinced that we had hit on the right method.

Tests were carried out in an apparatus consisting of a tubular oven for high temperature decomposition, a transparent quartz tube of 6 mm diameter and 0.5 meter length, and micro-absorption bubblers of the Polezhaev type [see diagram]. SiF_4 was absorbed with distilled water.

Procedure. An aliquot of the fluoorganic compound in a small tube was cooled in ice and connected to the quartz tube, two micro-absorbers, each of which had been filled with 5 ml distilled water, were connected to the other end of the tube. When the temperature of the oven had reached 900°, the tap on the tube connecting the fluoorganic compound was opened, and the vapors distilled slowly through the system by means of an aspirator which could draw air through at the rate of 2 liters per hour. When 2 liters of air + vapor had been passed through the apparatus, the absorbers were replaced by new ones and 2 liters of pure air swept through. While this was being done, the cold end of the quartz tube was placed as near as possible to the combustion zone, in order to ensure complete vaporization of adsorbed SiF_4.

Silicon was then determined in the absorption solution by the color formed on formation of the blue silico-molybdate complex. The solution from each absorber was separately transferred to a flask of molybdenum glass and diluted with water in accordance with concentration determined on a scale. To each 4 ml of test solution measured out into the colorimeter tubes, 1 drop of 0.1 N H_2SO_4, and 0.1 ml of ammonium molybdate* were added, and after shaking allowed to stand for 5 minutes for the color of yellow silicon molybdate complex to develop. At the end of this period 1 ml of 5% tartaric acid and 0.1 ml of freshly prepared 1% ascorbic acid solution were added. After 20 minutes, the intensity of the blue color was measured by comparison with a set of standards containing various amounts of chemically pure sodium silicate treated as described above.



The Na_2SiO_3 solution which was used for preparing the standard series contained 0.02 mg SiO_2/ml.

The series of standards used are given in Table 1.

Results of the tests on the weights given below of volatile fluoorganic compounds are given in Table 2.

TABLE 1

Standard solution (ml)	Corresponding amount of Si (mg)	Distilled water (ml)
0	0	4.0
0.06	0.0006	3.94
0.13	0.0012	3.87
0.25	0.0023	3.75
0.38	0.0035	3.62
0.50	0.0047	3.50
0.63	0.0059	3.37
0.75	0.0070	3.25
0.88	0.0082	3.12
1.00	0.0093	3.00

TABLE 2

Amount taken (mg)	Amount found (mg)	Amount found (%)
6.6	6.70	101.5
7.8	7.65	98.0
8.0	7.60	95.0
8.0	7.65	95.6

In order to simulate the actual problem — determination of small amounts of fluoorganic vapors in air — the experimental conditions were modified to carry out measurements on given concentrations of the vapor in the gaseous phase.

A drop of liquid, the weight of which had been previously determined, was introduced into a 9-liter flask fitted with a ground glass stopper with two tubes — a short and a long one. The taps on the outlet tube were closed and by slight heating the substance was vaporized. The 9-liter flask was then connected to an apparatus whereby the mixture of air plus vapor could be expelled from it. This was achieved by passing a saturated solution of NaCl into the flask. NaCl solution was fed in by a siphon from a measuring cylinder.

All the other experimental conditions, combustion of test material in quartz tube, absorption of SiF_4 and subsequent determination of Si, were the same as in the first series.

By conducting the tests in this way it was possible to measure out very small amounts of substance into the gaseous phase and to study the best methods for testing and subsequent treatments of test samples.

The results of Table 3 show the agreement between amount of sample taken and amount actually determined, and also the reproducibility of the results.

TABLE 3

Air drawn through in ml	Amount of test material in mg	Amount determined in mg
500	0.80	0.86
300	0.48	0.48
100	0.16	0.153
100	0.16	0.153
50	0.08	0.076
500	0.457	0.57
500	0.457	0.428
300	0.274	0.23
150	0.137	0.135
150	0.137	0.160
100	0.0915	0.084
100	0.0915	0.088

TABLE 4

Substance in mg	
Passage through 5% NaOH	Without alkali
0.80	0.765
0.335	0.325
0.450	0.428
0.153	0.153
0.084	0.088
0.076	0.076
0.069	0.068
0.069	0.065

Since it is possible that HF may be present in the air as well as the vapors of volatile fluoorganic compounds we carried out an independent series of determinations in which the gas-air mixture entering the oven was first sucked through 5% NaOH. Parallel experiments in which the air-vapor mixture was not scrubbed with 5% NaOH but in which all other conditions were identical showed that dilute NaOH is quite a suitable absorbent for HF as Table 4 shows.

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* 18.8 g of chemically pure ammonium molybdate was measured into a 250 ml flask, dissolved in water, and 80 ml of 10 N H_2SO_4 added and the volume made up to the mark.

SUMMARY

A method has been worked out for the determination of vapors of fluoorganic compounds in air. It is based on the combustion of the substance in a quartz tube at 900°; the SiF_4 formed is absorbed in water and is determined colorimetrically via silicon by means of the silico-molybdate complex. The air is removed into an evacuated gas pipet or bottle and forced into the combustion apparatus by means of saturated NaCl solution.

If HF is present in addition to fluoorganic compounds, the vapor-air mixture is passed through gas scrubbers filled with dilute NaOH before going on to the combustion furnace.

This scheme of analysis for volatile and gaseous fluoorganic compounds should be capable of application to a number of cases.

Because of the large variety of fluoorganic compoundsand their individual characteristics, however, it would be better to carry out an experimental check on each one individually, using concentrated material.

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P-ANISIDINE — A SENSITIVE REAGENT FOR CUPRIC CATIONS

A. Kh. Batalin

p-Anisidine or the methyl ether of p-aminophenol $H_2NC_6H_4OCH_3$ is a solid which melts at 57° and boils at 240°. It dissolves readily in organic solvents, but is not so soluble in water. Aqueous solutions are the most stable. Solutions of p-anisidine in organic solvents rapidly turn brown in the air, aqueous solutions can be stored without any significant change (in dark bottles) for 3-5 months. Aqueous solutions were used in most of the experiments described below.

p-Anisidine, like other amines, gives a number of characteristic changes on reaction with cupric cations. Experiments have shown that the character of this reaction changes in the presence of alkali metal halides and thiocyanates. Accordingly, mixtures of the reagent with these compounds were also tested.

The reagent was prepared by adding 1 ml of a saturated solution of p-anisidine in water to 10 ml of water. The reagent in admixture with halides or thiocyanates ("thiocyanate", or "iodide", or "bromide" reagents) was prepared by adding 1 ml of a saturated solution of p-anisidine in water to 100 ml of 0.1 N halide or thiocyanate. 2-3 drops of reagent solution are sufficient to give the corresponding reactions with 1 ml of 0.1 N solution of Cu^{2+}.

When aqueous solutions of p-anisidine react with Cu^{2+} cations, a yellow-green precipitate is initially formed, which rapidly turns brown and, after 5-8 minutes, acquires a dark-violet color. Solutions of low concentration of Cu^{2+} are colored a violet color, on addition of reagent no precipitate is formed. The yellow-green precipitate formed on addition of a drop of mineral acid also acquires a brown color. The sensitivity of the p-anisidine–Cu^{2+} reaction is fairly high — about 4 μg in 1 ml. Iron, silver, mercury, and oxidizing anions interfere.

The reaction is different when "thiocyanate" or "iodide" reagents are used; in such cases, dark red precipitates are formed when the cupric solution is concentrated, while the solution becomes a cherry color when the cupric concentration is low. The precipitates (or solutions) obtained keep their color for 10-15 hours, and hardly change at all when heated to 100°. The color of the precipitates or solutions is removed on addition of ammonia, citrates, pyrophosphates and addition of a large excess of mineral acid. The sensitivity of the "iodide" or "thiocyanate" reagents for cupric ions is very high-ca. 0.6 μg/ml, so that the limiting dilution is 1:600,000.

It is of interest to note that the "chloride" reagent only gives an effect when there is a large excess of chloride present. The "bromide" reagent gives a fairly definite reaction, but this must also be done in the presence of a large excess of bromide.

Experiments have shown that the sensitivity of the reaction for cupric ions is not diminished even in the presence of a 500-fold amount of Mn, Al, Zn, Mg, Ni, Cr, alkaline metals, alkaline-earth metals, and Fe^{2+}; a 50-fold amount of Co, Ag, Sn, uranyl, Ce, Hg^{2+}, Pb, and 5-fold amounts of Sb and Hg. Greater amounts of indifferent ions lead to a sharp reduction in the reaction sensitivity.

For qualitative detection of Cu^{2+} in the presence of Fe^{3+} and in the absence of oxidizing agents the masking action of NaF is used. To the test solution is added a saturated solution of NaF and a few drops of a "thiocyanate" reagent. In the presence of cupric ions the solution acquires a red-violet color, or if large amounts of cupric ions are present, a dark red precipitate is formed. The reactions are best carried out in a neutral or weakly acid medium pH 6.8-6.9.

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DETERMINATION OF INDICATOR ERROR BY THE KORENMAN METHOD FROM THE WEIGHT OF SUBSTANCE

I. L. Teodorovich

[The V.M. Molotov Tashkent Medical Institute]

In the determination of the indicator error by Korenman's method* two volumes of the solution to be titrated are measured out, one of which should be twice or (n)** times the other [where n is a whole number].

When a dry substance is used it is practically impossible to weigh two aliquots on a micro-balance so that one is an exact number of times more than the other. We therefore took two weights m_1 and m_2 such that $m_2 \approx 2m_1$ and dissolved them in known volumes of water, an equal amount of indicator was then added to each.

m_2 was titrated first, water was then added to m_1 so that at the end of titration the volume of liquid in both vessels was approximately equal.

If a is the amount in mg-equivalents in m_1, Δa and Δ the indicator error expressed in mg-equivalents and ml respectively, $b = m_2/m_1$, and v_1 and v_2 the volumes of solution with normality Nx in mg-equivalents/ml used for titrating m_1 and m_2 respectively, then

$$a + \Delta a = v_1 Nx. \qquad (1) \qquad\qquad b \cdot a + \Delta a = v_2 Nx. \qquad (2)$$

Multiplying (1) by b, determining Δa from (1) and (2) and dividing by Nx we get

$$\Delta = \frac{bv_1 - v_2}{b-1}\ \text{ml}. \qquad (3)$$

I.M. Korenman's formula is written in a similar form suitable for calculation. Results determined by formula (3) are adduced below

Determination of the Normality of NaOH Solution by Titration with Potassium biiodate.

Normality of NaOH solution	Weight of $KH(IO_3)_2$	$b = \frac{m_2}{m_1}$	Indicator	NaOH used in ml	Indicator error in ml NaOH	Corrected volume of NaOH in ml	Normality calculated for NaOH solution
0.0100	4.481	–	Methyl	1.20	+0.07*	1.13	0.01017
0.0100	10.816	2.414	red	2.80		2.73	0.01016
0.0200	5.160	–	Phenol-	0.75	+0.08*	0.67	0.01975
0.0200	9.398	1.821	phthalein	1.30		1.22	0.01976

* The positive errors in both examples are explained by a special case of formation of complex biiodate aquo-acids.

Received April 18, 1951

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* I. M. Korenman, Factory Labs. 1, 32, (1936).

** I.M. Korenman did not point out that n is a whole number. In all the examples given however n was equal to two.

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CRITICISM

Reply to A. K. Babko's Criticisms of the Article, "The Quantitative Determination of Trivalent Iron with Tetraborate" (J. Anal. Chem. 7, 280 (1952)

Since our work is of an original nature and includes a new direct method for the determination of Fe^{3+}, in which it was postulated that new, complex iron compounds were formed, we are glad of the opportunity to discuss the problem and are accordingly grateful for the chance to reply to criticisms of this question.

Babko's criticisms, however, are not a valuable contribution to the discussion, particularly in view of his far-from-scientific way of putting forward his views. In turning to the basis of the criticisms made, we, on our part, have the following to say.

First of all, Babko's fundamental observation that the electrode which we used was the wrong one, in connection with which he reproached us for "disregarding the fundamental theoretical postulates of the theory of potentiometric titration", is inappropriate for the following reasons.

Babko suggests that we should have used as standard electrode an electrode whose potential depends ina definite way on the concentration of one of the reacting ions, in particular the Pt electrode in the system Fe^{2+} - Fe^{3+}. This electrode, however, as well as a number of others (including the quinhydrone and the iron electrode) were studied by us in detail before we decided to use the Pt/Pt-black electrode for the potentiometric titration of $Fe^{3+}$with borate. According to our results, both Pt electrodes gave similar results for the titration, but since the smooth Pt electrode required 5-10 minutes for the potential to be established, while the Pt/Pt-black electrode took only one minute and seemed to be more sensitive, we decided to use the latter. The behavior of the Pt electrodes in our system can be represented as follows: a solution of an Fe^{3+} salt always contains traces of Fe^{2+}, i.e., solutions of Fe^{3+} salts are oxidation-reduction systems. The measurement of the potential of Pt electrodes in solutions of Fe^{3+} salts during their potentiometric titration with borate is determined on the one hand by a decrease in the concentration of Fe^{3+} ions during the process in which they are gradually linked up into fairly stable complex compounds, and on the other hand by oxidation of Fe^{2+} by aerial oygen adsorbed by the platinum. The excess of borate added after the equivalence point creates an alkaline medium so that when the $Fe(OH)_2$ takes the adsorbed oxygen from the platinum electrodes to form $Fe(OH)_3$ a sharp potential jump occurs. A completely analogous picture has been observed on a smooth Pt electrode in the system $Ag^{+}-Ag_2^{2+}$. In order to show that the concentration of Fe^{2+} in the solution actually affects the electrode potential, we potentiometrically titrated Fe^{3+} with borate in the presence of various amounts of Fe^{2+} and also measured the potentials of the Pt electrodes on addition of increasing amount Fe^{2+} to them.

An increase in Fe^{2+} concentration leads to a large decrease in electrode potential.

Babko's main objection is therefore removed.

With regard to Babko's other criticisms we say that some of his assertions contradict facts that are well known in chemical literature.

Thus, Babko affirms that excess of a coordinating ion leads to formation of more stable complex compounds, while our results agree completely with the conclusion of A. K. Babko and coworkers who determined the instability constants of a number of complex iron compounds, from which it was obvious that with increasing concentration of the coordinating ion the stability of the complex compounds decreased, e.g., in Babko and Kleiner' article. **

$$K_{[FeCNS]^{2+}} = 5 \cdot 10^{-3};\ K_{[Fe(CNS)_2]^{+}} = 10^{-1.96};\ K_{[Fe(CNS)_3]} = 10^{-1.4};$$

$$K_{[Fe(CNS)_4]^{-}} = 10^{0.8}$$

or in Babko's article. ***

$$K_{[FeSal]^{+}} = 4 \cdot 10^{-17};\ K_{[FeSal_2]^{-}} = 4 \cdot 10^{-12};\ K\ [FeSal_3]^{3-} = 2 \cdot 10^{-6}$$

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* A. Obrucheva, J. Phys. Chem. 11, 473 (1938)

** A. K. Babko, K. E. Kleiner, J. Anal. Chem. 1, 106 (1946)

*** A. K. Babko, J. Gen. Chem. 9-10, 745 (1945)

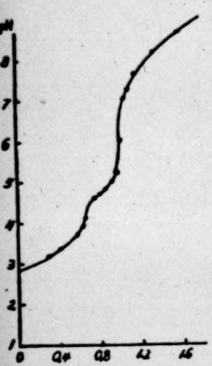
We got similar results:

$$K_{[FeB_4O_7]^+} = 1.78 \cdot 10^{-17}; \quad K_{[Fe_2(B_4O_7)_3]} = 0.7 \cdot 10^{-22}.$$

The appearance of a precipitate during titration of Fe^{3+} with borax on addition of an excess drop of borax after the equivalence point is explained by the fact that Fe^{3+} in solution $[Fe_2(B_4O_7)_3]$ is of the order of 10^{-6} g-ion/liter, i.e., is at a concentration far greater than the $[Fe^{3+}]$ essential for the precipitation of basic salts and $Fe(OH)_3$, i.e., of the order of 10^{-10} g-ion/liter.

Babko without any foundation asserts that we did not determine the pH of the solution. We did, however, carry out a series of pH determinations which we were unable to publish because of lack of space. In the present reply, however, we have adduced a curve shoing pH changes during titration of Fe^{3+} with borax.

Babko also pointed out that it is a serious drawback that we only gave values of $\Delta E/D\Delta$ instead of the values of the potential itself. Surely Babko must be aware that there are three graphical methods of presenting the results of potentiometric titrations which are of equal value: (1) E against V; (2) $\Delta E/\Delta C$ against C and finally, (3) $\Delta F/\Delta V$ against V. We chose (1) (which is not included in the published results) and (3). (3) has been used in a number of chemical investigations in potentiometry and in our opinion deserves attention, particularly in those cases where large potential jumps are not observed.



ml of 0.1N $Na_2B_4O_7$

Babko also queries the dissociation constant of boric acid, although the value for this constant is given both in classical textbooks* and in various notebooks**. We find that the value is $K'_{H_2B_4O_7} = 10^{-4}$, i.e. it is equal to the dissociation constants of HCNS, HNO_2, etc. Consequently it can be assumed that $H_2B_4O_7$ exists in weak acid solutions.

Babko doubts that we obtained five complexes. Apparently he does not understand that it is only the first two jumps that characterize the formation of iron borate complexes while the other three indicate the progressive decomposition of the complexes with the formation of basic salts; this is confirmed by the results of Table 1 in the article (p.290). From this table it should be clear to any one precisely how the complexes gradually decompose, and how many BO_2^- groups are contained in the basic salts. As regards the first jump on the curve, a similar intermediate jump has also been observed during the titration of aluminum salts with borates, and not only with borates but also with NaF***. It is incomprehensible why Babko is so hostile to the method we adopted. In each case he does not give any basis for his objections. We have based our conclusions on numerous experimental results and not on some preconceived belief or unbelief in them.

As regards Babko's observations re the simultaneous titraton of Fe^{3+} and Cu^{2+} we have the following to say: if one is to agree with Babko's opinion that during titration with borate, formation of basic salts and of ferric hydroxide occurs then on titrating a mixture of Fe^{3+} and Cu^{2+}, and taking into account the solubility products of the respective hydroxides $Fe(OH)_3$ should be precipitated first, followed by $Cu(OH)_2$. This is, however, in complete contradiction to experiment. Cu^{2+} is titrated first possibly forming basic salts and $Cu(OH)_2$ (solubility product = $5.6 \cdot 10^{-20}$) while Fe^{3+} is only titrated afterwards with formation of soluble complex compounds.

Moreover Babko's hypothesis re formation of a colloidal solution of basic salts during the first titration stage of Fe^{3+} ions with borate is impossible because we observed a similar type of titration not only during titration of aqueous but also of water-alcohol solutions of Fe^{3+} and also of its complex salts: ferric- salicylate, acetate, fluoride and thiocyanate, respectively. In addition, one may point out for Babko's information that even when obviously colloidal solutions are formed during volumetric reactions, then, in Dumansky's opinion, intermediate complexes are first formed the composition of which become more complex with time and leads to the formation of products of a colloidal nature.

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*I. M. Kolthoff and V. A. Stanger, "Volumetric Analysis", 1, 305 (1950)

**Chemists' Notebook 3, 493 (1952)

***I. L. Teodorovich, J. Anal. Chem., 7, 175 (1952)

Babko accuses us of not determining the equilibrium concentration of boric acid which is essential for calculation of the instability constants of the complexes. It would be of interest to know why Babko decided that we did not use this value. In our calculations of the instability constants of the complexes we naturally could not but determine the equilibrium concentration of boric acid since the value of the equilibrium concentration is essential for the calculations. We could not, however, put all these calculations in our paper because the amount of material required would be sufficient to fill an article on its own. Moreover, by the very nature of the article as printed, it is the conclusions to be drawn from them and not the calculations as such which are of interest. If the editor is prepared to print the caculations they are welcome to have them at any time.

The cryoscopic method served purely as a confirmation of complex formation during interaction between Fe^{3+} and borate. Babko is rather too insistent about "the neglect of the elementary rules of evaluating the accuracy of results" in which a curve was drawn on the basis of 17 observations. It is necessary to note that the tabulated results are not the results of one experiment but are the means of a whole series of replicate determinations, which is the usual method adopted.

We consider that what we have said above disproves Babko's observations re the nature of the work, and in particular his opinion about the unsuitability of the electrode which we used. Babko's conclusion that the work is of little value occasions surprise, since in his remarks the author subjects to criticism only individual sections of the work and keeps quiet about a number of other important aspects of the work which are very important for an understanding of the nature of the work as a whole.

In passing, we should like to note that at the moment we are studying compounds of a similar type and the results obtained confirm over and over again the participation of $B_4O_7^{2-} \rightleftarrows 2BO_2 \cdot B_2O_3$ in the inner sphere of the complex, equally with other addenda.

Babko's critique is methodolgically incorrect, since it is impossible on the basis of the questions which he has taken up to draw conclusions as to the incorrectness of aspects of the work which he does not understand.

M. B. Shchigol and N. B. Burchinskaya

January 12, 1953

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YU. A. CHERNIKOV

Recently Professor Yu. A. Chernikov, one of the outstanding specialists in analytical chemistry, a Stalin Prize Winner, and a Doctor of Chemical Sciences, celebrated his 60th birthday and the 30th year of his scientific activity.

Chernikov has devoted most of his attention, and still does, to the development of the analytical chemistry of the rare elements. This branch of analytical chemistry is one of the most complex and one of the least studied. The exciting development of industry in the Soviet Union, in particular that of the rare elements constantly requires analysts to develop analytical methods for the raw materials, the manufactured products, and also methods of phase control.

Chernikov during the first years of his scientific activity has strenuously struggled to solve these problems. One of the lines along which he has worked is the development of the theoretical and practical bases for the determination of small amounts of material. For this purpose he has very successfully used colorimetric methods involving the use of various organic reagents such as dithizone, diethyldithiocarbamate, hydroxyquinoline, etc., which ensure the highest sensitivity, accuracy and simplicity. A number of other physico-chemical methods of analysis has been widely developed under his leadership, e.g., internal electrolytical methods, potentiometry, etc.

The methods of analysis developed by Chernikov have been widely used not only in laboratories working on the rare elements but also in ferrous and non-ferrous laboratories.

During his many years in analytical chemistry Chernikov has educated many talented young specialists in this field. His students have defended many theses of great scientific and theoretical interest.

In addition to his scientific work he has also done a large amount of social-scientific service. He is a member of the Commission on Analytical Chemistry of the USSR Academy of Sciences, and a member of the Scientific Society of the Vernadsky Geochemical and Aanlytical Chemistry Institute. He also participates in the work of the J. Anal. Chem.

He was awarded a Stalin Prize in 1947 and the Order of Lenin in 1951 for his work.

The Commission on Analytical Chemistry of the USSR Academy of Sciences and the editorial board of the J. Anal. Chem. hope that Chernikov will be able to continue his successful and fruitful work in the development of analytical chemistry.

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UKRAINIAN CONFERENCE ON CHEMICAL CONTROL IN THE METALLURGICAL AND METAL-WORKING INDUSTRIES

A conference of Ukrainian analytical chemists organized by the Ukrainian branch of the Mendeleev All Union Chemical Society was held at Dnepropetrovsk from the 31st of May to the 4th of June, 1952.

The 277 delegates who attended the conference came from 10 regions of the Ukrainian SSR, from 20 towns – Kiev, Kharkov, Dnepropetrovsk, Stalino, Lvov, Zaporozhe, Krivoi Rog, Voroshilovgrad, Zhdanov, Gorlovka, etc. The delegates represented 72 organizations – 47 factories and 25 scientific research, educational institutions and other organizations. A number of scientific reports devoted to basic chemical control of metal quality was read at the conference.

In Professor A. K. Babko's report (Kiev) on "Colorimetric Methods of Analysis for Control in the Metallurgical Industries" the development of analytical methods in connection with the development of industry and increased demands for improved metal quality was considered.

A. K. Babko clearly demonstrated the prior claims of Russian scientists in the development of colorimetric analytical methods and their application to production control. He gave a brief review of methods of determining contamination in ferrous and non-ferrous metals, and formulated basic problems of further development and introduction of colorimetric methods for metallurgical production.

The necessity of a critical examination of the methods used for determination of silicon and phosphorus in metals and of antimony and arsenic in non-ferrous metals was noted.

S. A. Guskinskaya (Stalin Steel Institute, Moscow) read a report on "The Application of Mathematical Statistics in Analytical Chemistry" in which she explained how to work out results and evaluate them more accurately. She showed by means of many examples that using mathematical statistics it is possible to calculate not only random errors, which determine reproducibility, but also the deviation of results of individual determinations, and to establish the presence of systematic errors which determine the correctness of the analysis.

S. A. Guskinskaya gave suitable formulas and tables for getting results by the treatment of only a relatively small number of observations which characterize the observed phenomena to the same accuracy as the more complex classical methods of mathematical statistics used hitherto

V. S. Rossikhina and [illegible] L. Tsvkory (Dnepropetrovsk State University) in their report on "An Experiment on the Application of Spectral Methods for the Analysis of Materials, Slags and Ores" showed considerable success in developing spectral methods in the USSR and its application to production control.

The report dealt with work carried out at Dnepropetrovsk State University on attempts at introducing methods of quantitative spectral analysis into the work of factory laboratories in the Dnepropetrovsk and Zaporozhe areas. A spectrographic method has been developed by the authors for the analysis of copper, iron, manganese, magnesium, and silicon in aluminum alloys. Spectrographic methods for the analysis of rustless steel, iron ore, slag, etc., were also given. All the methods were tested on apparatus of Russian make and have been successfully introduced into production.

Engineers E. A. Nechaeva and O. Ya. Orlova (Petrovsk. Metallurgical Factory, Dnepropetrovsk) read a paper on "The Determination of Non-Metallic (Slag) Inclusions in Ferrous Metals" which included a description of an improved method for studying non-metallic inclusions. In the improved method, the apparatus which is used for the individual separation of the unstable manganese compounds in the anode residues is modified. The method for the removal of ferric oxide was also improved. Photocolorimetric methods were used for the determination of the chemical compositions of a whole series of stable non-metallic inclusions. The importance of petrographic methods for the study of non-metallic inclusions in metals was demonstrated, as well as the advantages of spectrographic methods in combatting flaws in metal ingots and in finished metal products.

Gurevich (Ukrainian Institute of Metals, Kharkov) in his report on "Chemical Methods for the Determination of Non-Metallic Inclusions and Gases in Carbon Steels", stated that electrolytic methods are the most complete and reliable methods for the separation of metallic and non-metallic phases. The author dealt with of inclusions of manganese oxide, the removal of sulfur inclusions in manganese and iron, the removal of ferrous oxide from electrolyte residues, and the determination of non-metallic inclusions stable in dilute HCL. The authors suggested a method for the removal of non-metallic inclusions from carbon steels based on lowering the acidity of the electrolytic bath used for electrolysis.

Yu. I. Usatenko and engineers E. L. Grenberg and V. I. Kopeliovich in their report on "Photocolorimetric Determination of Aluminum in Steel with "Stilbazo" without Preliminary Removal of Iron" gave details of the method they used for the photocolorimetric determination of aluminum using a new reagent "Stilbazo" synthesized by Soviet chemists. The method has a very great advantage, viz., the possibility of determining aluminum in the presence of many other elements. The method has been introduced into factory practice.

Reports were read by workers of the analytical section of the Dnepropetrovsk State University on the application of photocolorimetry to metal and ore analysis.

V. I. Reznik dealt with the use of phototurbidimetric titration for the analysis of dolomites and limestones and to the study of the precipitation reactions of magnesium, calcium, aluminum, iron and other metals;

V. D. Vasilenko devoted his paper to the application of photocolorimetric methods to the "non-destructive" analysis of metals and proposed a method of this type for the determination of manganese in carbon steels, and low alloy steels and casts. He also proposed a method for the determination of iron in copper and aluminum alloys. The experimental results were compared with results of spectrographic and gravimetric methods and also with specification tests and gave satisfactory agreement.

L. S. Sedyuk suggested a method for the determination of nickel and cobalt in manganese ores – a problem of considerable interest at present. Nickel determination is based on its separation from manganese by internal electrolysis with subsequent photocolorimetric determination with dimethylglyoxime in alkaline media, while cobalt is determined with nitroso-R-salt.

V. F. Maltsev and V. Ya. Sych (Tube Institute, Dnepropetrovsk) in their paper on "A Rapid Electrolytic method for testing steel for intercrystalline corrosion," critically examined existing methods of determining intercrystalline corrosion and proposed a new, rapid method for its determination.

The following papers were also read. –

"Rapid Analysis of Martensite and Foundry Slag", (F. G. Druzhinin-Stalin Metallugical Factory, Stalino); "Photocolorimetric Determination of Chromium in Slag", (V. A. Begma and V. I. Zhuravskaya-Karl Liebknecht Factory, Dnepropetrovsk). "A Rapid Method of Estimating Manganese in Ferromanganese and in Manganese Ores", (A. P. Belyaeva-Petrov Factory, Dnepropetrovsk), "Determination of Lead by Internal Electrolysis Using an Aluminum Anode", (B. Ya. Barko, Dnepropetrovsk); "The Application of Ionites (Ion Exchange Resins) for the Determination of Boron in Alloys and Certain Electrolytes", (Ya. A. Degtyarenko, Lvov Polytechnic Institute), "Determination of Slag Basicity by Means of Basicity Meters", (S. M. Tarashchanskaya, Voroshilovgrad) "Oxidation of Manganate to Permanganate by Persulfate without Using $AgNO_3$", (I. M. Malkin, Dnepropetrovsk Metallurgical Institute; "Some Analytical Properties of di-Betanaphthylthiocarbazone and its application for the Determination of Zinc and Iron Ores", (A. S. Grzhegorzhevsky, Dnepropetrovsk Metallurgical Institute) "Metallic Iron in Laboratory Tests for Ores and Other Materials", (N. F. Tkachenko, Krivoi Rog "Gikyuzhruda") "Organization of Work in the 'Red Star, Factory Chemical Laboratory", (M. G. Berdyrskaya, Kirovograd).

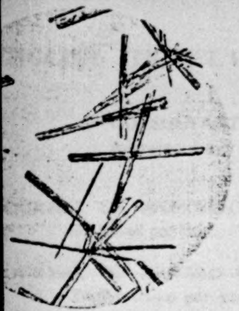
21 papers were read in all at the confernce, 10 of the papers by factory representatives and 11 by members of Scientific Research Institutes.

The conference established that Soviet analytical chemists have achieved considerable successes in organizing work in factory chemical laboratories, and in introducing advanced physico-chemical and physical methods of production control.

New gravimetric, volumetric, colorimetric and other methods have been developed by various institutes, factories, and mining laboratories which can be widely used in practice.

At the end of the conference the participants unanimously adopted a resolution in which detailed recommendations were given for further improvements in analytical laboratories. The successful realization of the resolutions of the conference must be carried out by all analytical chemists in factories and institutes of the Soviet Ukraine, who can contribute greatly to the fulfilment of Comrade Stalin's plans for building a communist society.

Microcrystalloscopic Reactions for Cyanides (page 185)



.4-Ethylbenzylaminophenyl-
mercury cyanide.

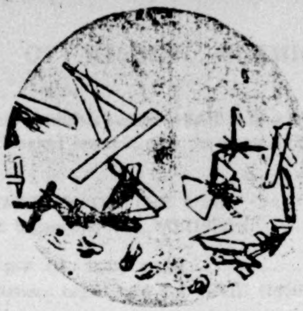


Fig. 2. Reagent – 1.4-ethylbenzylamino-
phenylmercuryacetate.

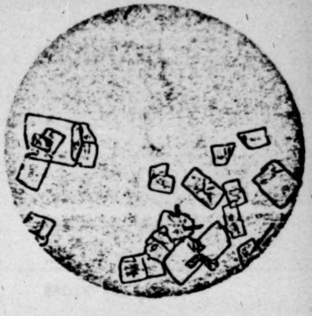
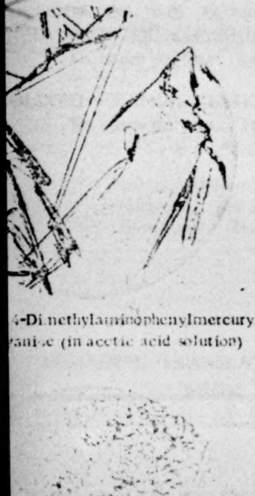


Fig. 3. 1.4-Dimethylaminophenylmercury-
cyanide (in aqueous solution).



4-Dimethylaminophenylmercury-
vanide (in acetic acid solution)

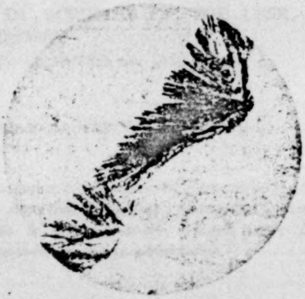


Fig. 5. Reagent – 1.4-Dimethylamino-
phenylmercury acetate.

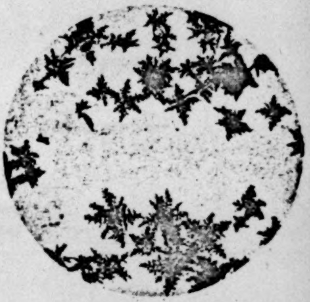
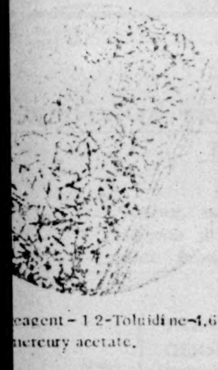


Fig. 6. 1,2-Toluidine-4,6-dimercury-
cyanide.



eagent – 1 2-Toluidine-4,6-di-
nercury acetate.

Thermal Analysis with Registration of the Volume of Gas Evolved (page 171)

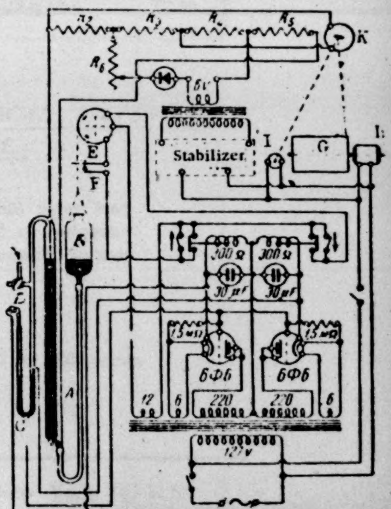

R2
R3
R4
R5
K
R6
6V
Stabilizer
I
G
I1
E
F
K
300 Ω
300 Ω
30 μF
30 μF
15 мΩ
15 мΩ
6Ф6
6Ф6
12
6
220
220
6
127v
B
A
C

Fig. 1.

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CHROMATOGRAPHIC ANALYSIS

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The V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry

On the 8th of March, 1903 Mikhail Semenovich Tsvet reported to the Biological Section of the Warsaw Naturalists' Society his discovery of the new chromatographic method. His report was published the same year in the Proceedings of the Society (1903 Vol. 14, pp. 20-39) under the title "A new category of adsorption phenomena and their application to biochemical analysis". Although a number of observations adduced by M. S. Tsvet relating to the discovery of the highly effective chromatographic method had already been noted in a number of his earlier articles, March 1903 is now accepted as the date of this noteworthy discovery. 50 years have elapsed since that time. These years, particularly the last 25 years, were years during which the chromatographic method has been widely developed, improved, and used in an ever increasing number of fields of knowledge and technics. Soviet scientists have contributed significantly to the development of chromatographic methods and have succeeded in unravelling the theoretical bases of chromatography, and worked out more effective and expedient methods for applying chromatographic techniques. An attempt has been made in the present article to point out the significance of chromatographic methods in analytical chemistry and to indicate some characteristic examples of its application in this field.

The analysis of mixtures has been, and still is, the main field of application of the chromatographic method. In order, therefore, to evaluate the significance and position held by chromatography in analytical chemistry it is necessary to consider the general features and basic tendencies in the development of analytical chemistry itself.

In the course of the intensive development of analytical chemistry, side by side with the ever increasing interest displayed in the determination of traces of material and in the analysis of very small amounts of material [1,2], two tendencies have become more apparent; the selective determination of a given component in a complex mixture and the selective separation of a definite component from a mixture. Colorimetric methods are graphic examples of the selective determination of one component in a complex mixture. On the one hand, one should note the switch-over from determination of naturally colored components to the use of highly sensitive reagents which can give intensely colored compounds with the component sought for. This method of approach, the basis of which was laid by M. A. Ilinsky and L. A. Chugaev, is, at the present time being successfully developed by V. I. Kuznetsov [3-5], while on the other hand, the technique of colorimetric determination is being continuously improved; a change over from simple colorimeters of the Duboscq type by means of which the colors of one-component systems can be compared, to photocolorimeters and to spectrophotocolorimeters which increase the selectivity of colorimetric methods considerably and enable colored compounds to be determined when they are present together [6].

One of the greatest achievements in the development of instrumental methods is X-ray spectral analysis based on a study of X-ray spectra which are practically independent of the presence of other materials [7,8]. In principle, determinations carried out by means of radioactive indicators are independent of the composition of a mixture and of experimental conditions.

For all methods of this group, the presence of specific means of identifying the components and the determination of their concentrations are characteristic for each of them. Thus, in spectroscopy the wave-length characterizes the nature of a component, while the line intensity determines its amount; in polarography, the nature of a component can be determined from its half-wave potential, while its amount is given by wave-height, etc.

Methods for selective isolation of particular components from a mixture are related to their conversion into another phase; of these methods it is sufficient to mention precipitation, distillation, and extraction [9,10]. Each of these methods has its own particular advantages and disadvantages; thus, extraction techniques yield very pure products, but only a comparatively small number of substances is amenable to such treatment (particularly selective extraction). Precipitation of difficultly soluble compounds is one of the oldest methods (gravimetric analysis), few elements, however, can be isolated by this technique and the purity of the products obtained is not always high, because of side reactions (co-precipitation, occlusion, etc.) [11]. Distillation can only be applied to the separation of fairly volatile components which differ appreciably in their vapor pressures; distillation has hardly been used at all up to the present in inorganic analysis.

Chromatography belongs to this second group of methods which involves the selective isolation of a particular component [12]; in chromatography also we have either a transfer of the components to be determined into the sorbent phase (partition chromatography, ion exchange) or the formation of a special phase by the component (adsorption chromatography). The absence of specific indices of the nature and amount of component is general for all methods of this group. Thus, both during precipitation, distillation, and extraction the nature of the individual components is established by specific reactions, just as are their amounts. This fact is completely obvious and needs no clarification. Nevertheless in the field of chromatography the question of the possibility of a direct and purely chromatographic determination of the amount of a component is not always clear enough and is seldom discussed in the literature. A number of experimental papers [13, 14], have been devoted to an explanation of the relation between zone height on a chromatogram and the concentration of the substance to be analyzed in solution. The results of these experiments are not very reassuring. Only in individual cases, and even then only with a low accuracy which is determined not only by the difficulty of measuring zone height, but also by other considerations of a much more fundamental character, has it been possible to establish the required relation. The reason for this, which follows from the simple theory of chromatographic dynamics [15], is that the substance on the chromatogram zones is unevenly distributed; thus, in the case of a convex isotherm in adsorption chromatography, most of the material is found in the front part of the zone and only a small part of it is found in the form of a "tail" in the upper part. The picture is the reverse when the isotherm is concave. It is natural that the unequal distribution of the material in the zone excludes the possibility of comparing the total zone height with the amount of component being analyzed. It may be considered, therefore, that the theory of chromatography and also accumulated experimental data have completely confirmed what M. S. Tsvet said: "The question arises whether it is impossible for the chromatographic or chromatoscopic method to be transformed into a chromatometric method which can express the respective amounts of components in a mixture by the heights of the "adsorbed zones" determined by them, i.e. determining them in 'adsorption equivalents'. Experiments carried out by myself along these lines did not give satisfactory results, and theoretical considerations indicate that the proposed relation between the amount of pigment being determined and the height of adsorbent column occupied by it does not exist" [16]. Thus, the application of chromatography in chemical analysis follows the aim of isolating particular components for their subsequent identification and determination of their amounts by chemical, physical, or physico-chemical methods.

Chromatographic technique is very simple and has changed comparatively very little since M. S. Tsvet's time. Improvements predominantly relate to automatic fractionation. The separation of a mixture of components which resemble each other in their properties necessitates the selection of a large number of fractions, and frequently takes a long time. This fact makes it expedient to use special apparatus which can carry out fractionation of the filtrates coming from the columns. A fairly large number of set ups for such a purpose has been described in the literature (vide, e.g. [17]) in which the set ups are operated either by changes in weight of the receivers with accumulation of filtrate, or when a definite number of drops has fallen into the receiver, etc. An apparatus which can be recommended was constructed by us about 2 years ago in conjunction with S. V. Kuzmin and V. A. Yanchevsky at the Institute of Geochemistry and Analytical Chemistry, (Figs 1 and 2). The principle of this apparatus is as follows: after given time intervals the apparatus, which is connected to an electric clock, switches on an electromagnet, the electromagnet in turn attracts a spindle connected by means of a cog mechanism to an axle on which the funnels arranged underneath the columns are fixed. The volume of filtrate taken is regulated by the outflow velocity of the solution from the chromatographic columns. Constant outflow velocity is ensured because the wash solution is kept in a flask of large volume similar to a Mariot flask. The use of such apparatus frees the worker from the necessity of supervising the experiment and enables him to work on a large number of columns simultaneously. The column dimensions can be varied through a wide range (Fig. 3)[1], the choice of column being determined by the amount of mixture to be handled.

For paper chromatography GEOKhI[2] uses a special cell in which the paper is suspended in a space saturated with the vapors of the solvent being used so as to stop the paper drying out.

The components of the test mixture can be conveyed along the sorbent layer by continuously passing through the column either the test mixture itself (frontal analysis), or a solution which does not contain the components of the test mixture (wash analysis), or finally, a solution containing a substance which is sorbed more readily than any of the components of the test mixture (displacement analysis). These three variants of chromatographic analysis are shown schematically in Fig. 4. It is pertinent to note that the displacement of gaseous components in the case of adsorption chromatography can be successfully carried out by gradually (from above downward) heating the column [18, 19].

In recent years a number of articles has been published [20,21], which describe how components of test mixtures were conveyed along the sorbent layer by applying a direct current to the ends of the chromatographic column. This approach is a development of S. I. Dyachkovsky's very interesting work [22], in which he suggested and worked out an electrocapillary method of analysis; the essence of the latter method is the application of an electric field to a piece of filter paper soaked with the solution to be analyzed.

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[1] See Plate, page 228.

[2] GEOKhI = Institute of Geochemistry and Analytical Chemistry. Publisher.

By means of chromatographic methods it is possible to separate mixtures of closely related organic compounds (Fig. 5) and also mixtures of rare-earth elements [23], and isotopes [24]. In these cases extremely small quantities (gamma amounts) can be handled and be completely extracted from the columns. The use of small amounts of test mixtures favors chromatographic techniques, since a decrease in specific loading (ratio of weight of test mixture to weight of sorbent) increases many times the elementary acts of separation. It is also expedient to carry out the process under conditions corresponding to an approximation of the system to equilibrium (low throughput solution velocity and small sorbent grains). The most diverse organic and inorganic mixtures, both colored and colorless have been separated by means of chromatographic methods.

M. S. Tsvet applied the method of chromatography which he developed for the separation of plant pigments and it is from this fact that the method derives its name. Nevertheless he was fully aware of the possibility of extending this method to colorless substances. His foresight has been clearly confirmed by all subsequent developments in chromatography; in its turn this necessitated developing other methods of observing chromatographic processes since in the case of colorless materials visual observation is naturally out of the question. In this connection one must first of all mention the illumination of chromatographic columns with ultra-violet light [25,26], in order to detect any luminescent substances. Sometimes resort has been made to converting colorless compounds into colored ones, either at the beginning of an experiment (running carboxyl compounds through a column at the same time as dinitrophenylhydrazine, or amines with picric acid, etc.), or directly after separation on the column itself (e.g., washing a column of colorless sorbent with a solution of ammonium sulfide or potassium ferrocyanide during the separation of certain cations, or the use of indicators for detecting zones occupied by organic acids). These methods however have a limited application: on the one hand many substances, e.g. the simplest hydrocarbons, do not give colored derivatives; while on the other hand the conversion of colorless compounds into colored compounds before chromatographic separation as a rule, essentially lowers the possibility of separating the components, since complexing the molecule smooths out differences in the properties of the primary components of the test mixture. These factors have attracted a great deal of work, in which it is suggested that fractionation of colorless filtrates be carried out instead of observing the chromatograms on the columns directly. Developments along these lines are also determined, as shown above, by the fact that a quantitative determination of the contents of the components in test mixtures cannot be carried out by measuring zone heights on the column, but requires direct methods of estimation after quantitative separation of the mixture.

Determination of filtrate composition or changes in its composition (which determines the expedient combination of individual samples) is carried out at the present by a number of methods. For separating a mixture of gaseous components measurements of refractive index or thermal conductivity of samples issuing from the column are often made.

In the case of colorless organic liquids, the refractive index of the filtrate is usually measured (best of all by means of an interferometer, since this shows up clearly the difference in refractive indices between filtrate fractions and the pure solvent passed through the column). The method of detecting the appearance of a new material in a filtrate by the formation of "diffusion striations" is of great interest [27]; the fall of a drop into a cell-receiver leads to the formation of a characteristic striation which is easily visible (using the requisite projection) on a screen. For the separation of mixtures of inorganic compounds, one has to resort to qualitative tests; nevertheless, the method involving determination of filtrate activities when small amounts of radioactive, labelled atoms are added to the mixture before separation is proving of inestimable value and is acquiring increasing importance. Radioactive indicators ensure the possibility of detecting component zones on chromatographic columns directly.

The universal use of chromatographic methods is based on the existence of four variants; adsorption, partition, ion-exchange, and precipitation chromatography. Each kind of chromatography has its own characteristic mechanism, which governs the nature of the sorbents to be employed.

The simplicity, efficiency, and universal applicability of chromatographic methods are the reasons for their wide application in chemical analysis. It is impossible to encompass all the variety of work carried out in chromatography within the framework of this article; we shall therefore only adduce below individual examples which are, however, as characteristic as possible, of the application of chromatography to the analysis of mixtures of the simplest organic as well as of inorganic compounds. The analyses of mixtures of biochemically important compounds will only be mentioned in very broad terms, in accordance with the general policy of the Journal of Analytical Chemistry.

ANALYSIS OF MIXTURES OF SIMPLE ORGANIC COMPOUNDS

Analysis of simple organic compounds can be carried out by adsorption, partition, and in part by ion-exchange chromatography. The choice of one or other variant of the chromatographic method for a given problem depends fundamentally on the nature of the components of the mixture. It is therefore natural that hydrocarbons can only be analyzed by means of adsorption chromatography. It is expedient to analyze mixtures of hydrocarbon derivatives which possess different polarities by means of partition chromatography. Finally, analysis of compounds which dissolve in water with subsequent dissociation into ions can be carried out by ion-exchange chromatography. One must take into account the fact that the best variant to use is determined by the possibility of bringing out to the greatest extent the differences in properties of the components of the test mixture. Thus the change in dipole moment of isomeric compounds or lengthening of the hydrocarbon chain in homologous polar derivatives of the alcohol type or organic acid type is most clearly expressed by changes in their solubility and not by changes in the extent to which they are adsorbed.

Solubility in water (g/100 g solvent)

Butyric acid	miscible	Normal	butyl	alcohol	7.36
Valeric acid	3.7	Sec.	"	"	12.5
Caproic acid	0	Tert.	"	"	miscible

In this case therefore it would be more convenient to use partition chromatography, whose efficiency is determined by the value of the partition coefficient (which is related to the solubility of the substance) between the immiscible phases.

ADSORPTION CHROMATOGRAPHY

The separation of mixtures by means of this chromatographic variant is determined by the adsorbability, which in turn is related to peculiarities in the structure and composition of a molecule. Physical adsorption is determined by the energy of intermolecular interaction - which is basically orientative and dispersive [28]. As a result, to the first approximation, the adsorbability of substances on a non-polar sorbent of the active charcoal type is determined by the polarizability of the adsorbate molecules. This means that the adsorbability of molecules which differ in composition but consist of the same atoms (e.g. hydrocarbons) increases with increasing molecular weight; when comparing the adsorbabilit of molecules of differing composition, the value of the polarization of atoms and bonds must be taken into account. On polar sorbents of the silica gel type adsorbability is determined both by the polarization and by the dipole moments. The value of the latter is particularly high in compounds with low polarizability (water, methyl alcohol, etc.). Molecular structure has also a considerable influence on adsorbability; thus, other conditions being equal, in order of adsorbability on active charcoal we get aromatic compounds first, followed by naphthenic and lastly paraffinic hydrocarbons.

Adsorbability depends basically also on the structure of the adsorbent, a lot of work has been devoted by M. M. Dubinin [29], to a study of the structure of activated charcoal; A. V. Kiseler has studied the structure of silica gel [30]. The adsorbents which have the greatest adsorption energy are adsorbents with small pores, and they accordingly find wide application for the chromatographic separation of substances which are not easily adsorbed.

The success of an experiment is very often dependent on the choice of solvent As a rule, the adsorbability of a solvent should be much lower than that of any of the components of a test mixture. This ensures that the resolving capacity of the adsorbent is brought out to its full. If the solvent adsorbability is very high, it is possible that the components of a test mixture may not be separated and will pass through the column into the filtrate.

A great amount of work has been done on the separation of organic mixtures by means of adsorption chromatography. We shall confine ourselves to a few examples.

The determination of total hydrocarbons in air can be carried out easily by converting them to carbon dioxide on a platinum wire followed by subsequent absorption of the carbon dioxide with alkali, and back titration of excess alkali with acid. The problem of separating individual hydrocarbons by purely chemical methods is practically impossible. It is better, therefore, to carry out a preliminary separation of such mixtures by means of adsorption chromatography. As has been shown in one of our papers [31], absorption of a mixture of the simplest hydrocarbons by a column of activated carbon of predetermined humidity and subsequent passage of pure air through the column leads to a quantitative separation of methane, ethane, propane, mixtures; methane came out in the first 400 ml of air, while no hydrocarbons were present at all in the next 400 ml of air; ethane came out after passing 1000-4000 ml of air; propane, under the conditions chosen by the author, was not removed from the column even when 10,000 ml of air had been passed through, and could only be stripped off the column by heating the column. Small variations in the ratios of the components in the original mixture, in the temperature and the air velocity through the column did not affect the degree of separation. Subsequent determination of individual components was carried out by combustion as described above.

E. A. Mikhailov and B. A. Kazansky have worked out and improved a chromatographic method of determining the content of aromatic hydrocarbons in admixture with naphthenic and paraffinic hydrocarbons. They showed [27], that on passing a test mixture through a column of industrial silica gel of small pore size and washing the column first with ethyl alcohol and then with water, initially only the naphthenic and paraffinic hydrocarbons pass through into the filtrate; the aromatic hydrocarbons appear considerably later. If the separation of the fractions is not clean cut enough, then they are recycled through the column and washed with pentane or isopentane. The authors separated the aromatics from the solvents by washing with water (to remove alcohol), or distillation (for removal of pentane).

PARTITION CHROMATOGRAPHY

The separation of mixtures by partition chromatography is determined by differences in the partition coefficients of the components between two immiscible phases, one of which (the "stationary phase") is located in the sorbent pores, while the other is the wash solvent ("mobile phase"). In most of the work carried out, hydrophilic substances such as silica gel (with coarse pores so as to decrease the adsorption effect) or starch have been used for holding one of the liquid phases; as a result of this, only water, or low molecular weight organic compounds with high dipole moments (methyl alcohol, nitromethane, etc.) can be used as the "stationary phase".

The efficiency of partition chromatography is basically decided by the choice of mobile and immobile phases. One must bear in mind that the possibility of separating a mixture and the simplicity of a determination are determined by the difference in partition coefficients. In this connection therefore it is obvious that the liquids for the two phases must be chosen so that the partition coefficients of the components of the test mixture between the mobile and stationary phases should be as different as possible in magnitude. As an example we shall quote the analysis of a mixture of fatty acids by means of partition chromatography.

V. L. Kretovich et al [32], chose industrial silica gel as well as silica gel prepared by themselves as sorbent. The immobile phase was water, while the mobile phase was a mixture of butyl alcohol and chloroform. To carry out their analysis the test mixtures were neutralized with 0.1 N alkali using phenolphthalein as indicator, and the whole evaporated to dryness on a water bath. The residue was treated with 1:1 sulfuric acid until the salts dissolved when sodium sulfate was added. The liquid was extracted 5 times with a 1% solution of butyl alcohol in chloroform. The solution thus obtained was transferred to a column which was then first washed with the 1% solution of butyl alcohol in chloroform until all the butyric acid had been extracted, and then with a 5% solution of butyl alcohol in chloroform to wash out propyl and acetic acids. The zone containing formic acid was mechanically removed from the column. The acids in the filtrates were determined by titration with 0.05 N NaOH.

N. A. Fuk's work on the determination of the gamma-isomer of hexachlorocyclohexane in technical products [33], and the analysis of mixtures of ammonia and amines [34] is of great interest.

The use of paper pulp and filter paper as sorbent in partition chromatography has in recent years become more widespread [35,36]. A detailed review of work in this field has been given in V. V. Pachinsky's article [37]. The use of "paper chromatography" for the analysis of inorganic mixtures will be described in a subsequent section.

Paper chromatography has been successfully used for the analysis of amino acid mixtures and of protein hydrolyzates [35,37].

Successful separation, as usual, for this method depends on the differences in the R_f values for the individual components of the test mixture, where

$$R_f = \frac{\text{rate at which substance moves}}{\text{rate at which solvent moves}}.$$

A mixture consisting of a small number of amino acids can be separated on a narrow strip by using one solvent (strip or uni-dimensional chromatography). While even when a large number of components are present (and differences in the R_f values are small), the mixture can be successfully separated, if the paper is used in conjunction with two organic solvents. An example of this type is the analysis of rabbit skin hydrolyzate [38] (the two dimensional chromatogram depicted in Fig. 6 was obtained). The individual spots were detected on the paper after development with a 0.2% solution of ninhydrin [1) aspartic acid, 2) glutamic acid, 3) serine, 4) glycine, 5) lysine, 6) arginine, 7) alanine, 8) histidine, 9) hydroxyproline, 10) proline, and 11) valine]. By means of this method [39] it was shown that when l-aspartic acid is decarboxylated by micro-bacteria α-alanine is formed. Carnosine and anserine were also detected in heart muscle [40].

In order to increase the efficiency of chromatographic separation on paper, a number of authors have used an additional factor – an electric field [41, 42]. By using an electric field it has been found possible to separate glutamic acid from arginine, and aspartic acid from lysine.

A large number of articles is now available in the literature on the combined chromatographic – ionophoretic method [43,44].

ION-EXCHANGE CHROMATOGRAPHY

Separation by means of ion-exchange chromatography (see below) is dependent on differences in the capacities of the ionic components to exchange with mobile sorbent ions. In one sense ion-exchange chromatography can be of significance only for the separation of organic compounds, such as organic acids, which dissociat in aqueous solution. Nevertheless, the analysis of mixtures of certain organic compounds in which the chemical interaction of the mixture components with specially prepared ion-exchange materials is used, is of interest and opens up new perspectives.

The separation of mixtures of amino acid, vitamins, and alkaloids is based on the following principle. It was found [45], that a salt is formed between the basic amino groups and the acid form of a cationite (cation-exchange resin) e.g.:

$$\mathrm{RH + NH_2 \cdot CHR'\text{-}COOH \rightleftharpoons RNH_3 \cdot CHR'\text{-}COOH.}$$

Cationites in their calcium and sodium forms do not react with amino acids. Anionites (Amberlite IR-4B and deacidite) react with dicarboxylic acids (but not with mono-carboxylic acids) according to the scheme:

$$\mathrm{RNH_2 \cdot HX + HY \rightleftharpoons RNH_2 \cdot HY + HX,}$$

where $\mathrm{RNH_2 \cdot HX}$ is the anionite: HY – any amino acid.

Glutamic and aspartic acids have been separated by means of ion-exchange resins [46]. Various methods and apparatus have been proposed for the separation of amino acids [47,48].

The use of chemical interaction between an ion-exchange resin and the test mixture components may be illustrated by the separation of alcohols or organic acids from aldehydes and ketones and the separation of mixtures of the latter. Aldehydes and ketones form α-hydroxysulfonic acids on interaction with bisulfite.

$$\mathrm{RCHO + HSO_3^- \rightleftharpoons RCHOHSO_3^-; \qquad R_2CO + HSO_3^- \rightleftharpoons R_2COHSO_3^-.}$$

It has been shown [49], that on passing an aqueous solution of a mixture of ethyl alcohol and furfural or other aldehyde in the bisulfite form through an Amberlite IRA-400 column, and washing the column with a small amount of water, the ethyl alcohol passes through into the filtrate; in order to extract the furfural a solution of sodium carbonate plus bicarbonate is passed through the column. The experimental error does not exceed 1%. By simple modifications of the experimental conditions it was found possible to separate organic acids from aldehydes and ketones [50], and to separate mixtures of aldehydes and ketones [51].

ANALYSIS OF MIXTURES OF INORGANIC COMPOUNDS

Inorganic mixtures can be analyzed by means of ion-exchange, partition, or precipitation chromatography. The choice of which variant to use depends on the nature of the test mixture components, and on the conditions under which differences in the properties of the components to be determined can be shown up to their best advantage.

Relatively speaking, ion-exchange chromatography is the variant most widely used. Partition chromatography is of importance for compounds which under suitable conditions can be brought into the organic phase. In this sense there is a complete analogy between partition chromatography and extraction, with the essential difference that by means of partition chromatography it is possible after one experiment to isolate a number of components from a mixture in a pure state, even when the components have very similar properties. Precipitation chromatography, the basic principles of which have only been formulated fairly recently, has hitherto found only limited application [52,53].

ION-EXCHANGE CHROMATOGRAPHY

At an early stage in the development of the chromatographic method, comparatively unstable cationites, often of variable composition, were used in ion-exchange compounds; e.g. silicates, zeolites, silica gel, Fuller's earth, etc. Nevertheless, even when these materials were used, it was found possible to determine certain cations easily, particularly those of the heavy metals when present simultaneously. By passing the test solution through chromatographic columns filled with a colorless ion-exchange compound (clay, silica gel, etc.) and subsequently washing the column, separate zones were obtained which, on treatment with reagents (ammonium sulfide, etc.), could be converted into colored zones. Schwab [54], using this method, got the following arrangement for a series of ions:

$$\begin{array}{lllllllll}
\mathrm{As^{3+}} - & \mathrm{Sb^{3+}} - & \mathrm{Bi^{3+}} - & \mathrm{Cr^{3+}} - & \mathrm{UO_2^{2+}} - & \mathrm{Pb^{2+}} - & \mathrm{Cu^{2+}} - & \mathrm{Ag^{+}} - & \mathrm{Zn^{2+}}. \\
 & & & \mathrm{Fe^{3+}} & \mathrm{Co^{2+}} & & & & \\
 & & & \mathrm{Hg^{2+}} & \mathrm{Ni^{2+}} & & & & \\
 & & & & \mathrm{Cd^{2+}} & & & & \\
 & & & & \mathrm{Fe^{2+}} & & & &
\end{array}$$

The sequence changes essentially when the ions are first converted into the ammoniate complexes of the metals:

$$\begin{array}{lllll}
\mathrm{[Co(NH_3)_6]^{2+}} - & \mathrm{[Zn(NH_3)_4]^{2+}} - & \mathrm{[Cd(NH_3)_4]^{2+}} - & \mathrm{[Ni(NH_3)_6]^{2+}} - & \mathrm{[Ag(NH_3)_2]^{+}}. \\
 & & \mathrm{[Cu(NH_3)_4]^{2+}} & &
\end{array}$$

In recent years the sorbents used in the practical application of ion-exchange chromatography to chemical analysis have been invariably synthetic organic ion-exchange materials and they have practically replaced inorganic ion-exchange materials (aluminum oxide, permutite, zeolites) and sulfonated coal. The synthetic organic ion-exchange compounds [55-57] which are condensation or polymerization products excel all other ion-exchange materials in their exchange capacity, particularly under favorable experimental conditions (acid or alkaline media) and are reasonably chemically stable and mechanically durable. The high capacity of ion-exchange materials depends on their accessible volume. The fact that even at present, methods of synthesizing ion-exchange materials possessing increased capacity with regard to particular elements are being mapped out is also of great importance. In this connection particular attention should be drawn to V.A. Klyachko's work [58], in which he synthesized a number of selective cationites by introducing during the condensation stage sodium ethylene diamine tetracetate (for calcium absorption), dimethylglyoxime (for nickel absorption) and chromotropic acid (for absorption of titanium, gold, vanadium, etc.).

The large variety of Russian cationites and anionites which is being turned out at present on the laboratory and also on the semitechnical scale make the comparative testing of ion-exchange materials with a view to selecting the most promising material for a particular analytical problem of vital importance. Some results obtained by the present authors on the basic characteristics of Russian and foreign ion-exchange materials were published in conjunction with K. V. Fillippova in 1952 [59]. It was shown there that in selecting an ion-exchange material one must give preference to those which have the highest exchange capacity at the pH determined by the nature of the test mixture. The character of the relation between exchange capacity and the pH which was experimentally established by potentiometric titration is determined by the nature of the ionic group of the ion-exchange material. Thus, the exchange capacity of sulfonated cationites (RSO_3H) is practically independent of the pH of the solution, while for cationites containing the carboxyl group ($RCOOH$), the capacity increases essentially with increasing pH; finally, cationites with hydroxyl groups can only undergo ion-exchange reactions in alkaline media. Since in a large number of cases ionic groups of different types can be present simultaneously in cationites, it follows that experiments with cationites should be carried out in media which are as basic as possible. On the other hand the exchange capacity of anionites is realized to its fullest extent in acid media.

At present, synthetic ion-exchange resins are being applied at an increasing rate in analysis. Though ion-exchange chrommatography cannot be regarded as an independent method in analytical chemistry, it is nevertheless an exceedingly important intermediate stage in analytical processes which ensures the isolation of particular elements from the mixture being analyzed.

THE ISOLATION OF CATIONS AND ANIONS DURING THEIR DETERMINATION

Determination of iron, aluminum, magnesium and other ions in the presence of sulfate and phosphate is a very complex analytical problem. The results obtained in practice suffer from fundamental errors and the analytical procedure is very lengthy. The position can be radically changed if the cations are separated from the anions, since their determination can be carried out subsequently by well known and simple methods.

Such a separation is easily effected by means of cationite columns. Thus, on passing a test solution through a column charged with a cationite in the H-form (RSO_3H), cations are separated from anions according to the scheme:

$$2RSO_3H + MeSO_4 \rightleftharpoons (R{-}SO_3)_2Me + H_2SO_4,$$

where Me = Fe, Mg, etc.

As a result of the exchange reaction the cations become joined to the active cationite groups. Sulfate and phosphate anions pass through into the filtrate and after the column has been washed with distilled water, can be determined by normal methods.

The adsorbed cations can be easily removed by washing the column with dilute HCl. The removal of cations from the resin can be represented by the scheme:

$$(R{-}SO_3)_2Me + 2HCl \rightleftarrows 2RSO_3H + MeCl_2.$$

After washing the column, all the metals will be in the form of their chlorides in this second filtrate; in this form they can be easily determined.

On washing the column with HCl, the cationite is reconverted into the H-form, and is ready for further use.

Determination of the sulfate ion as barium sulfate, which at first glance seems to be a simple problem, does not always give the right results, because of coprecipitation of ions of magnesium, sodium ammonium, etc., which might be in the solution, with the $BaSO_4$. A preliminary separation of sulfate with an ion-exchange resin excludes such errors and also simplifies and speeds up the determination. On passing the test solution through a cationite in its H-form, the sulfate comes through as sulfuric acid, which can be determined by titration with alkali or can be determined gravimetrically as $BaSO_4$. The application of cationites, however, is not always successful. E.g., we observed that if chromium or copper are present in solution, then part of the sulfate is held back by the cationite because of coordination compound formation. At the same time, part of the metal passes through into the filtrate as a complex chromium anion. We found that preliminary addition of ammonia to the test solution rectifies matters, since the complexing capacity of ammonia is greater than that of sulfate ions. As a result, copper and chromium are held back by the cationite in the form of complex cations.

This method of separating ions may be used for routine analysis of table salt for its chloride content. On passing the solution through a column filled with a cationite in the H-form, HCl passes through into the filtrate, and this can be titrated with alkali.

$$RSO_3H + NaCl \rightleftarrows RSO_3Na + HCl,$$

These methods have already found wide practical application. Some authors [60-62] have determined the concentration of salt solution containing NaCl, Na_2SO_4, $NaNO_3$, $Cu(NO_3)_2$, etc. by titration of the respective acids obtained on passing the salt solutions through cationites in their H-form with alkali.

This technique can be used as an indirect method of determining the moisture content of salts. The principle of this method is to determine the true salt concentration in solution by titration of the acids formed on passing the salt solution through a cationite in its H-form with alkali. The difference between true salt concentration and the concentration calculated on the basis of weight of salt originally taken corresponds to the moisture content of the salt. In principle it is possible to use both cationites and anionites for the determination of moisture content by the chromatographic method. In the case of anionites, it is of course alkali that is formed and titrated.

An aliquot of the test solution is passed twice through a column of KU-1 cationite in the H-form. The column is then washed with a large amount of distilled water. The wash water is combined with the filtrate and the whole titrated with 0.5 N sodium hydroxide. The moisture content is given by the formula:

$$B = \frac{(c_3 - c_2)}{c_3} \cdot 100\%,$$

where $c_2 = \frac{c_1 V_1}{V_2}$; c_1 is the sodium hydroxide concentration; V_1 is the volume of sodium hydroxide used for titration; V_2 is the volume of salt solution passed through the column; c_2 is the true concentration of salt in the original solution; and c_3 is the concentration of salt in the original solution, calculated on the basis of the weight taken. This method determines total water, both hygroscopic and crystallization.

According to G. E. Kurilchikova, this method for determination of the moisture content of any salt gives results with errors of ± 1%. Comparison of this method with others leads us to hope that the rapid and simple chromatographic method will find use in analytical practice.

The use of cationites for the determination of sulfate ions in raw, feed, and drinking water, has been described by a number of authors [63-68]. Effective methods have also been worked out for the determination of phosphate by means of cationites [69-70].

Polarographic determination of sulfates cannot be carried out in the presence of iron, aluminum, cobalt, manganese, and zinc. This problem, however, has now been solved by removing these metals by using a cationite [71].

CONCENTRATION AND SEPARATION OF CATION MIXTURES

For the analysis of raw water and waste water from factories, in which the usual practice has been to concentrate by evaporation in order to get sufficient of the components being tested for, it is better to filter the water through columns filled with cationites or anionites.

Filtration through columns filled with a cationite in its H-form can be successfully applied to the determination of metal ions, e.g., copper and other ions in milk [72], various wines, and fruit juices.

In many instances the conjoint use of concentration on a column with a polarographic finish gives excellent results for the determination of traces of metals [73], in objects of animal or plant origin.

Amphoteric metals can be removed quantitatively from anions and non-amphoteric cations by absorption with cationites and subsequent extraction from the column with alkali. Zinc, aluminum, antimony, molybdenum, and tungsten were removed in this way from the basic hydroxides of iron, copper, and other metals [74]. This method has an essential advantage over the usual alkali separation, since extraction of ions by the hydroxides is eliminated.

The chromatographic separation of chromium and manganese from iron is based on the oxidation of the first two elements to the negatively charged CrO_4^{2-} and MnO_4^- ions, respectively, while iron remains as Fe^{3+}. On passing such a mixture through a cationite column only Fe^{3+} is retained, while chromium and manganese pass into the filtrate.

Zirconium and hafnium [75], can be separated from other cations by forming non-associated, electrically neutral molecules of $ZrO(NO_3)_2$ and $HfO(NO_3)_2$, so that on treatment of a test mixture with nitric acid all other metals remain as simple cations and on filtering through a column, are retained on the absorbent while the zirconium and hafnium pass through into the filtrate.

In the analysis of native platinum, separation of platinum group metals from other contaminants (iron, copper, etc.) can be effected by dissolving the test samples in aqua-regia, whereby ions of different charge are formed [76]; all the platinum group metals appear as complex anions $[PtCl_6]^{2-}$, $[PdCl_6]^{2-}$, $[RhCl_6]^{3-}$, $[IrCl_6]^{2-}$, and are not retained on the sorbent on passing through a column containing a cationite in the H-form; iron, copper, and other contaminants under these conditions remain as simple cations, and are held back by the active group of the cationite.

The different complex forming capacities of various elements forms the basis for a wide range of methods for isolating different elements from mixtures in analytical practice.

By using a 5% citrate solution at pH 1.6, iron can be converted into a complex anion of the composition $[FeCit_2]^{3-}$, which can pass through a cationite as the ammonium salt and can thereby be separated from aluminum which remains as a simple cation Al^{3+} under these conditions [76]. The aluminum is retained on the column and can be subsequently washed off for determination by the usual method.

At higher pH's aluminum, just like iron, forms a complex citrate anion $[AlCit_2]^{3-}$, and will therefore pass into the filtrate. It is on this fact that a method of separating calcium and magnesium from iron and aluminum in the analysis of ores has been based [77]. Under these conditions calcium and magnesium are absorbed by the cationite.

Molybdenum can be conveniently determined in ferromolybdenum by an ion-exchange method. Both metals are found in the form of charge ions MoO_2^{2+} and $[FeCl_3]^{3-}$ in HCl solution. On passing the solution through sulfonated coal in the H-form iron passes into the filtrate, while the molybdenum is subsequently extracted with alkali.

Another example [78], of the separation of this pair of metals in the analysis of ferromolybdenum is the use of a mixture of phosphoric acid and ammonia, with which only the iron forms a stable complex of the apparent composition $[Fe(PO_4)_2]^{3-}$ which is retained on a column of aluminum oxide. Molybdenum as well as vanadium pass into the filtrate.

Ion-exchange chromatography has considerably simplified the analysis of copper-iron ceramic alloys and bronzes [79]. The separation of copper from iron is based on differences in the stability of their pyrophosphate complex compounds. As a result of successive treatment of the test solution with pyrophosphate and ammonia (pH 10-11) the metals to be resolved are found in different ionic states; iron as the complex anion $[Fe(P_2O_7)_3]^{6-}$, and copper as the cation $[Cu(NH_3)_4]^{2+}$.

Filtration of the solution through a column of SBS cationite in the H-form leads to quantitative separation of iron from copper.

Copper and aluminum were successfully separated under the same conditions by changing the complexing agent. Aluminum in a mixture of tartaric acid and ammonia forms the complex anion $[Al(C_4H_4O_6)_3]^{3-}$; while copper remains as the complex cation $[Cu(NH_3)_4]^{2+}$.

When it is necessary to separate copper from iron and aluminum a mixture of salicylic acid and ammonia (pH 10) is employed. Under these conditions iron and aluminum form the complex salicylate $[MeSal_3]^{3-}$; while copper remains as the cuprammonium ion $[Cu(NH_3)_4]^{2+}$, and on filtering the solution through a column is retained by the cationite.

A simple separation of mixtures containing manganese and iron is based on their varying capacities to form complex compounds with ammonium oxalate at pH of 5. Under these conditions only iron forms a complex anion $[Fe(C_2O_4)_3]^{3-}$; manganese remains as the simple cation Mn^{2+} which is held back by a cationite in the H-form.

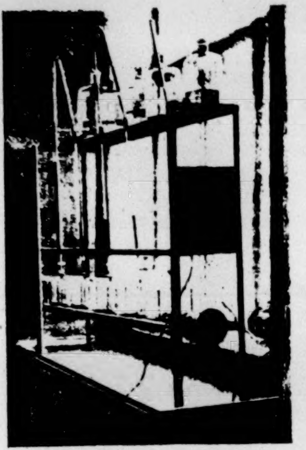


Fig. 1. An apparatus for the automatic fractionation of 5 small columns.

Fig. 2. An apparatus for automatic fractionation of 2 columns of average size.

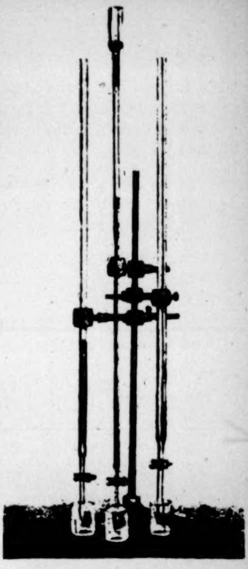
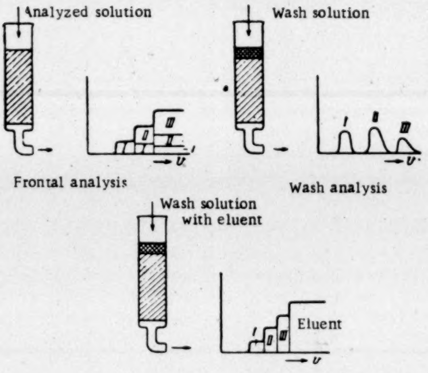


Fig. 3. Chromatographic columns.



Analyzed solution
III
II
I
v
Wash solution
I
II
III
v
Wash solution with eluent
I
II
III
Eluent
v

Frontal analysis

Wash analysis

Eluent analysis

Fig. 4. Three methods for carrying out chromatography.

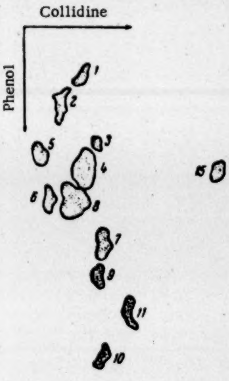


Fig. 5. Paper chromatogram of procollagen from rabbit skin.

V. Osipova separated iron from chromium by a preliminary treatment of the solution with thiocyanate. Only chromium forms a stable complex compound with an anion of composition $[Cr(SCN)_6]^{3-}$; iron remains as a simple cation and is held by the cationite KU-2 in the H-form on passing the solution through a column.

Ion-exchange resins have been successfully used for separating alkaline-earths and rare-earth elements. A number of papers has been devoted to this question [23, 80, 81]. A mixture of the dissolved salts of the rare earths is absorbed by the upper layer of the column filled with cationites of the Amberlite and Dowex type, and is then washed with a dilute solution of organic acids (citric or tartaric). The extent to which the mixture is resolved depends essentially on the concentration of the complexing agent and the pH of the solution. In this way even such closely related pairs as praseodymium and neodymium have been resolved.

Separation of rubidium and cesium was effected on Dowex-50 by washing the column with 0.15 N hydrochloric acid. Ion-exchange resins have been used for the extraction and isolation of nuclear fission products [23,82]. On passing mixtures through cationites in the H-form (Amberlite IR-1, IR-100 or Dowex-50) a complete separation of cations from anions has been made. By modifying the preliminary treatment and the washings of the column, individual radio-isotopes have been isolated from their mixtures and identified.

Mixtures can be separated on the basis of differences in the basicity and acidity of its components. It has been shown [83] that chloride and sulfate ions can be easily separated by passing the mixture of the respective acids through an anionite. Sulfate ions are absorbed in the upper part of the column.

By choosing a suitable ion-exchange resin which is acid or basic enough, respectively, to neutralize any one of the components of the mixture, it is easy to separate weak acids (HCN, H_2S, phenols, carbon dioxide and salicylic acid) from strong acids (HNO_3, HCl, H_2SO_4, etc.), by passing the mixture through a weakly basic anionite capable of neutralizing only strong acids.

Ion-exchange resins have been used for determining the instability constants of complex compounds [84,85], for purifying chemical reagents [86], and for the preparation of demineralized water which can be used successfully to replace twice distilled water.

PARTITION CHROMATOGRAPHY

A large amount of work has appeared in recent years in which paper is being used more and more frequently as the carrier for the immobile phase. The successful application of this method depends wholly on the quality of the paper used. Special types ("paper for chromatography") are prepared using pure cellulose as a base, and special methods are used for processing it in order to ensure freedom from mineral contamination and to give a homogeneous layer. The paper prepared in this way can have varying densities. Watmann No. 1 and No. 2 are the types most widely used abroad. Of the Russian types of paper, filter paper (blue ribbon), the so-called basis of "crab parchment", and also a special type of chromatographic paper (No. 3) developed by TsNIIB can be used for chromatographic analysis.

Paper chromatography is very simple. A drop of the test mixture is placed on a strip or sheet of paper. The paper is placed in a special container saturated with vapors of the solvent being used. The strip or sheet is lowered into a bath containing an organic solvent saturated with water. When separation is complete (the liquid front has moved 30-50 cm) the paper is dried and developed with special reagents.

When sheets of paper are used, after drying they are turned through 90° and the other edge of the paper lowered into a second solvent which produces a further separation of the mixture because the zone velocities in different solvents vary. The paper is then dried and developed with suitable reagents. The chromatogram obtained is a pattern of spots on the paper. The analysis of a few alloys are given below as examples.

An alloy containing platinum, palladium, gold, silver and copper was dissolved in aqua-regia; after removal of excess acid by evaporation the residue was diluted with water [87]. A drop of this solution was placed on a test paper, n-butyl alcohol containing 1 N hydrochloric acid being used as the solvent. The mixture of n-butyl alcohol and hydrochloric acid was also used for the separation of a mixture of aluminum, gallium, indium and zirconium [88].

Gold in admixture with the platinum metals [89], can be separated by using methyl-n-propyl ketone plus hydrochloric acid as the mobile solvent. The gold zone moving at the same speed as the solvent comes first, the mixed platinum + palladium, and rhodium + iridium zones come behind.

By using methyl-n-propyl ketone and acetone plus hydrochloric acid, cobalt, copper, iron, manganese, and nickel [88], can be separated. Nickel, cobalt, and copper zones are developed with rubeanic acid, the manganese zone with silver nitrate, and the iron zone with potassium ferrocyanide.

M. Lederer [90], carried out systematic measurement of the R_f coefficients for the majority of the metals; he used butyl alcohol saturated with 1 N hydrochloric acid, or 10% nitric acid, or 10% and 20% hydrogen bromide respectively as mobile solvents.

A method has been described [91], for the quantitative separation of cadmium from copper alloys.

The behavior of cations with respect to various mixtures of solvents, both pure solvents and ones containing complexing agents [92,93], has been studied by a number of authors. These same authors have described methods for the qualitative analysis of mixtures of lead, silver, mercury, iron, tin, strontium, barium, cadmium, cobalt, nickel, bismuth, arsenic, antimony, calcium, aluminum, etc. They used butyl alcohol + benzoylacetone as solvent; R_f values are given for a number of anions (chlorides, bromides, nitrates, etc.).

Vanadium can be separated from admixture with other components by using ethyl ether or tetrahydrosylvene + nitric acid and hydrogen peroxide. 8-Hydroxyquinoline can be used as the developer in this instance.

A large amount of work has been done on the paper chromatography of nickel, cobalt, copper, aluminum, iron and titanium [94]. The author has shown how it is possible to separate these components both by the use of pure solvents (acetone, benzene, dioxane, and a number of alcohols, etc.) and by the use of mixtures of these solvents with hydrochloric acid, formic and other acids. This work is mainly of a qualitative nature. The following mixtures were separated: 1) nickel-copper; 2) copper-cobalt; 3) nickel-cobalt; 4) iron-titanium; 5) iron-aluminum; 6) titanium-aluminum.

Recently a thesis by Eliseeva was published [95]. On the basis of literature results and also from her own work on Russian chromatographic paper, the author gives a table of R_f values for 40 cations using 10 solvents. The possibility was demonstrated of separating a mixture of metals precipitated by pyridine at a pH of 6.5 (aluminum, chromium, iron, titanium, zirconium, and uranium) by using two solvents successively; methyl butyl ketone containing 2.5% nitric acid and ethyl alcohol containing 10% of 5 N hydrochloric acid. By using two-dimensional chromatograms, cations precipitated by 8-hydroxyquinoline were separated. In this case butyl alcohol brought to equilibrium with 2 N hydrochloric acid and acetone containing 5% water and 8% hydrochloric acid were used as solvents.

Despite the universal use of "paper chromatography" which enables the most diverse substances (both organic and inorganic) to be determined, its essential drawback is the impossibility of using it for the separation and isolation of large amounts of material. This can be overcome by using chromatographic columns filled with cellulose pulp [36].

The use of ethyl ether containing 5% nitric acid as a solvent for the determination of uranium in minerals and ores enables a rapid, simple and accurate method to be worked out for the quantitative separation of this element [96]. The main difficulty is the preparation of the cellulose pulp. Results are given in the literature for the use of briquettes prepared beforehand. V. K. Sarygina prepared pulp as follows for a number of experiments. The crushed cellulose (if possible, not containing any mineral contaminants) is allowed to swell and then boiled with distilled water containing (3-5%) nitric acid. In this way a homogeneous mass containing filaments of a particular size is obtained. By varying boiling time, pulps with varying filament sizes (which determines the throughput through the column) can be obtained (i.e. a pulp with a definite degree of beating). The pulp is finally freed from nitric acid by washing with distilled water. In order to get a homogeneous mass in a dry state, the pulp is worked up with alcohol and ether. This treatment also serves as an additional method for freeing the cellulose from a number of contaminants.

The column is prepared as follows: the tube is first filled with the solvent to be used and small amounts of the dry paper pulp are introduced. In order to get the densest possible layer, the top of the column is left open during all the filling operations, solvent being added as necessary.

In the case of analysis of mixtures whose components are only soluble in water, one should soak a small amount of dry paper pulp with the solution being used and place it on the top part of the column. Direct introduction of the aqueous solution destroys the homogeneity of the pulp and leads to its "coiling up". Preliminary results on the separation of salt mixtures gave completely satisfactory results.

Such are the basic features of the application of chromatography in analytical chemistry. It can be seen how chromatography which was originally designed for solving a specialized problem - viz, the composition of the pigments of green leaves, is, at present being widely used for the separation of the most diverse mixtures of organic and inorganic substances, the number of papers published each year increasing all the time. This is the best and clearest proof of the productivity of the ideas of our renowned compatriot Mikhail Semenovich Tsvet.

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THE CHROMATOGRAPHIC METHOD IN QUALITATIVE ANALYSIS

Part I

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M. S. Tsvet's chromatographic adsorption method [1], has, in recent years found wide application in organic and inorganic chemistry, in biochemistry, medicine and in other sciences and branches of industry. The theory of chromatographic analysis and its variants have been successfully developed.

Chromatographic adsorption of inorganic materials is still in its initial stages of study. E. N. Gapon has worked out a theory of ion-exchange chromatography [2-6], but the dynamics of ionic exchange has only been studied to a comparatively small extent. Individual examples of the separation of inorganic cations and anions are given in the literature, but as yet no systematic investigations have been made which would lead to the creation of an independent chromatographic method in qualitative analysis. There is no doubt that the development of a chromatographic method of qualitative analysis would also lead to the creation of quantitative adsorption methods.

It can be postulated that the characteristic features of the chromatographic method in analysis can be reduced to the following:

1) Many analytical operations which are difficult and require a lot of time to carry them out can be simplified considerably, and the time reduced by the use of chromatograms.

2) The use of selective adsorption can lead to a rapid separation of groups of cations and anions and also to separation of individual ions from complex mixtures; the grouping of cations and anions may be different to those of classical analysis, and the groups themselves may contain a smaller number of representatives which facilitate subsequent separation into individual components or even their detection.

3) The use of complex formation can lead to the separation of elements of similar chemical properties, e.g. alkali and alkaline-earth elements, etc.

By using differences in the instability constants of complex compounds at a given pH, the complexes can be separated from the general mixture.

4) By means of selective adsorption cations can be separated from such anions as SO_4^{2-}, PO_4^{3-} etc., while on the other hand cations which interfere with sulfate ion determination can be removed.

In order to apply the chromatographic method successfully in qualitative analysis it was necessary to clarify the adsorability of cations and anions on various adsorbents separately for each analytical group of ions as defined by the classical methods of qualitative analysis.

According to published material the study and compilation of an adsorption series of certain cations and anions on a small number of adsorbents has been carried out by a few authors. Schwab and coworkers in 1937 [7-14], were the first to describe the separation of cations by a chromatographic method in a column of Merck's aluminum oxide aluminate standardized by Brockman's method, and a separation of anions on a column of aluminum oxide given a preliminary treatment with nitric acid.

The adsorption series for cations from the top of the column downward was as follows:

$$H^+ > As^{3+} > Sb^{3+} > Bi^{3+} > \begin{array}{c} Cr^{3+} \\ Fe^{3+} \\ Hg^{2+} \end{array} > UO_2^{2+} > Pb^{2+} > Cu^{2+} > Ag^+ > Zn^{2+} > \begin{array}{c} Co^{2+} \\ Ni^{2+} \\ Cd^{2+} \\ Fe^{2+} \end{array} > Tl^+ > Mn^{2+}.$$

Schwab's adsorption series for anions on aluminum oxide was supplemented by Gapon and Shuvaeva [15] to give:

$$OH^- > PO_4^{3-} > C_2O_4^{2-} > SO_3^{2-} = [Fe(CN)_6]^{4-} = CrO_4^{2-} > S_2O_3^{2-} > SO_4^{2-} = [Fe(CN)_6]^{3-} =$$
$$= Cr_2O_7^{2-} > NO_2^- > CNS^- > I^- > Br^- > Cl^- > NO_3^- > MnO_4^- > ClO_4^- > CH_3COO^- > S^{2-}.$$

Schwab [10,16], also established a different adsorbability for complex ions obtained from solutions of ammonium and tartrate salts, on aluminum oxide. The adsorption series for the ammonium complexes were:

$$Co^{2+} > Zn^{2+} > Cd^{2+} \quad Ni^{2+} > Ag^+ > Cu^{2+},$$

while the adsorption series for the tartrate complexes were

$$Mn^{2+} = Cd^{2+} = Zn^{2+} = Co^{2+} = Ni^{2+} > Pb^{2+} > Cu^{2+} > Bi^{3+} > Fe^{3+} > Cr^{3+}.$$

Erlenmeyer and Dahn [17], proposed 8-hydroxyquinoline as an adsorbent and established the following sequence:

$$VO_3^- > WO_4^{2-} > Cu^{2+} > Bi^{3+} > Ni^{2+} \quad > \quad Co^{2+} > Zn^{2+} > Fe^{3+} > UO_2^{2+}.$$

According to Erlermeyer and Dahn, this sequence corresponds to the solubilities of the hydroxyquinolates in water. The authors explain chromatographic separation by the formation of hydroxyquinolates on the surface of the hydroxyquinoline crystals. As a result of the formation of the difficultly soluble vanadates and tungstates of hydroxyquinoline, both cations and anions are separated simultaneously on the given column.

T. B. Gapon and E. N. Gapon [18, 21], in 1948 established an adsorption series of cations on permutite prepared according to the Kurnako, Berg and Sveshnikova method [19]. The order of adsorption on permutite was found to be:

$$Hg^+ > Fe^{3+} > Hg_2^{2+} > Ag^+ = Pb^{2+} > Tl^+ > UO_2^{2+} = \begin{array}{c} Cu^{2+} \\ Zn^{2+} \\ Cr^{3+} \\ Co^{2+} \end{array} > Mn^{2+}.$$

Davydov and Lisovina [22], established the following adsorption sequence for a number of cations on bentonite:

$$Ca^{2+} > Ba^{2+} > Sr^{2+} > Mg^{2+}.$$

Published material shows that all the cations and anions which are met in the ordinary course of inorganic qualitative analysis have been studied during a study of adsorption series. Adsorption series for the alkali and alkaline-earth metals are not available, nor series for cations in groups 3,4 and 5. The same applies to anions.

The aim of our work was to establish adsorption series for cations and anions on a few adsorbents for each group of ions separately. This will enable methods to be worked out in the future for obtaining and developing colored chromatograms for the qualitative detection of cations and anions in a systematic course of analysis.

TABLE 1

Cation Adsorption Series on Various Adsorbents

Adsorbent	Adsorbtion series				
	Cations of the 5th group	Cations of the 4th group	Cations of the 3rd group	Cations of the 2nd group	Cations of the 1st group
Chromatographic aluminum oxide	$Al^{3+} > Sb_3{}^+ >$ $> Sn^{2+}$	$Bi^{3+} > Hg_2{}^{2+} >$ $> Hg^{2+} > Pb^{2+} >$ $> Cu^{2+} > Ag^+ >$ $> Cd^{2+}$	$Fe^{3+} = Cr^{3+} > Al^{3+} >$ $> Zn^{2+}$ $Co^{2+} = Ni^{2+} =$ $= Fe^{2+} > Mn^{2+}$	$Mg^{2+} > Ba^{2+} >$ $> Ca^{2+} > Sr^{2+}$	$K^+ > NH_4{}^+$
Permutite	Reacts chemically with adsorbent	$Hg_2{}^{2+} > Hg^{2+} >$ $> Ag^+ = Pb^{2+} >$ $> Cr^{2+} = Cd^{2+}$	$Fe^{3+} > Al^{3+} > Cr^{3+} =$ $= Zn^{2+} > Co^{2+} = Mn^{2+} =$ $= Fe^{2+} > Ni^{2+}$	$Mg^{2+} > Ba^{2+} >$ $> Ca^{2+} >$ $> Sr^{2+}$	$K^+ > NH_4{}^+$
Bentonite-Askangel	Ditto	$Hg_2{}^{2+} = Ag^+ >$ $> Hg^{2+} > Pb^{2+} >$ $> Cd^{2+} > Cu^{2+}$	$Fe^{3+} > Al^{3+} > Cr^{3+} >$ $> Fe^{2+} > Zn^{2+} > Ni^{2+} =$ $= Mn^{2+} = Co^{2+}$	Not studied	
Suifunite Nos. 55, 124,127	$As^{3+} > Sb^{3+} >$ $> Sn^{2+}$	$Hg_2{}^{2+} > Hg^{2+} =$ $= Bi^{3+} = Pb^{2+} >$ $> Ag^+ > Cu^{2+} =$ $= Cd^{2+}$	$Fe^{3+} > Al^{3+} > Cr^{3+} >$ $> Zn^{2+} > Co^{2+} > Fe^{2+} =$ $= Ni^{2+} = Mn^{2+}$	$Mg^{2+} > Ca^{2+} >$ $> Sr^{2+} >$ $> Ba^{2+}$	$K^+ > NH_4{}^+$
Bleached clay	Not adsorbed		Not adsorbed		
Talc	Not adsorbed		Not adsorbed		
Chalk	Reacts chemically with adsorbent	Reacts chemically with adsorbent		Not adsorbed	

ADSORPTION SERIES WERE STUDIED ON THE FOLLOWING ADSORBENTS

1. Commercial chromatographic aluminum oxide ground to a particle size of 0.25 mm. For the separation of anions the oxide was first washed with nitric acid and then with water until the filtrate was neutral.

2. Permutite-aluminosilicate containing water and which possessed ion-exchange properties, was first suggested as an adsorbent for the chromatographic separation of ions by E. N. Gapon, T. B. Gapon, and F. M. Shemyakin [20].

The permutite was prepared in the form of a gel by pouring solutions of sodium aluminate and sodium silicate together.

Aluminum oxide aluminate was prepared as follows; a solution of sodium aluminate was first made by interacting metallic aluminum turnings or powder with 30% sodium hydroxide. The amount of alkali used was in such excess as to ensure that all the dissolved aluminum was converted into aluminate and no undissolved precipitate of aluminum oxide remained. Usually 101 g of metallic aluminum was dissolved in 1 liter of 30% alkali in a 3 liter flask in view of the violent reaction which occurred and because of foam formation.

The solution of sodium aluminate thus prepared was filtered through a No. 3 suction filter and diluted with water to a concentration of ca.2% (calculated as aluminum oxide). Two volumes of the 2% sodium aluminate and 3 volumes of 2% sodium silicate (calculated as SiO_2) was then quickly mixed with vigorous agitation. The gel which was formed after 14 hours was freed from excess liquid on a Buchner funnel at room temperature. The dry gel obtained was ground up and washed free from excess alkali by washing first with cold and then with hot distilled water. Washing was continued until the pH of the wash water was 9.5-9.8.

TABLE 2

Anion Adsorption Series on Various Adsorbents

Adsorbent	Adsorption Series		
	Anions of the 1st group	Anions of the 2nd group	Anions of the 3rd group
Chromatographic aluminum oxide	$PO_4^{3-} > C_2O_4^{2-} > CO_3^{2-} > SO_3^{2-} = CrO_4^{2-} > S_2O_3^{2-} > SO_4^{2-} > Cr_2O_7^{2-}$	$I^- > Br^- > Cl^- > S^{2-}$ 1)	$NO_2^- > NO_3^- > CH_3COO^-$ 1)
Anionite NO	$S_2O_3^{2-} > CrO_4^{2-} > SO_4^{2-} > C_2O_4^{2-} > PO_4^{3-} > CO_3^{2-}$	$I^- > Br^- > Cl^- > S^{2-}$	$NO_3^- > CH_3COO^- = NO_2^-$
Anionite MMG-1	$C_2O_4^{2-} > PO_4^{3-} = S_2O_3^{2-} = CO_3^{2-} = Cr_2O_7^{2-} = SO_4^{2-}$	$I^- = Cl^- = Br^- > S^{2-}$	$NO_2^- = CH_3COO^-$ NO_2^-
Anionite TN	$CrO_4^{2-} > SO_4^{2-} > S_2O_3^{2-} = CO_3^{2-} = PO_4^{3-} > C_2O_4^{2-}$	$I^- > Cl^- = Br^- = S^{2-}$	$NO_3^- = NO_2^- = CH_3COO^-$

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1) The series was established by K. V. Chmutov and coworkers.

After washing, the permutite was dried to an air-dry state and ground in a mortar to the requisite particle size, i.e. 0.25 mm. The finer permutite particles and dust were removed by sieving.

3. Askangel-bentonite clay of a pale grey color. Origin Askan in the Azerbaidzhan S. S. R.

The Askangel was ground up and dried at 110-120° for 2-3 hours in order to increase its absorptive capacity. The fractions were those used with particle size 0.25 mm and those of smaller particle size.

4. Sulfunite Nos. 55, 124 and 127 - tuff ashes of a pale yellow color, origin Far East. Dust and fractions with grain size of 0.25 mm were used.

5. Bleached clay, pale yellow color, preliminarily dried for 2-3 hours at 110-120° and ground to a dust.

6. Kaolin, talc and chalk adsorbents of a white color ground to a dust.

7. Anionites (anion-exchange resins) NO, and MMG-1, TN - synthetic resins (The Mendeleev Chemico-Technical Institute). Anionites NO and TN are white in color while anionite MMG-1 is pale yellow. The ion-exchange resins were ground to a particle size of 0.25 mm, the very fine powder being removed by sieving, after which they were converted into the OH-form by saturation with 5% NaOH, and subsequently washed till the filtrate was neutral.

Determination of the adsorption series of the ions on various absorbents and also supplementation of series already established by other authors were carried out as follows.

Glass chromatographic tubes 0.5-0.6 cm in diameter and 10 cm long with an opening in the bottom covered with a small plug of cotton wool were filled with dry adsorbent preliminarily ground in a mortar and sieved to a particle size of 0.25 mm. The adsorbent was introduced into the column in small amounts after which it was tamped down first by tapping the tube on the table surface until settling finished, when it was compacted by means of a glass pestle. The adsorbent after packing occupied approximately half the volume of the column. The column was clamped in a stand. The test solution which was made by mixing equal volumes of two different salt solutions of equal concentration in a vessel was then pipetted on to the chromatographic column.

The solution was usually passed through the column at the rate of 200 ml/hour. Drops of filtrate issuing from the column were collected in beakers containing suitable reagents which were capable of giving characteristic reactions with the ions to be tested for. It was possible to judge the order in which the ionic zones were disposed on the chromatographic columns by the appearance of the characteristic reaction for the test ions.

The results obtained are given in Tables 1 and 2.

Cation adsorption series were studied on the following adsorbents (Table 1): chromatographic aluminum oxide, permutite, bentonite- Askangel, Suifunite Nos. 55, 124, and 127, bleached clay, talc, kaolin and chalk.

Anion adsorption series were studied on (Table 2) chromatographic anionic aluminum oxide, and the anionites NO, MMG-1 and TN.

Adsorption series for cations of the 3-4 groups on bentonite-Askangel, for cations of all groups on Suifunite and for cations of the 2nd and 1st group on chromatographic aluminum oxide and permutite are given in Table 1. The results show that the cation adsorption series was the same on the different varieties of Suifunite. Cation adsorption series on chromatographic aluminum oxide were supplemented to give

Sn^{2+}, Hg_2^{2+}, Fe^{2+} and Al^{3+}, and on permutite: Hg_2^{2+}, Fe^{2+} and Al^{3+}.

Preliminary experiments showed that it is better to study the adsorbability of magnesium ions in conjunction with the ions of the alkaline earth metals than with ions of the alkalis, as is usually done in classical analysis. Magnesium is therefore shown as a cation of the 2nd group in the table.

Separation of Group I cations on chromatographic aluminum oxide, permutite, and Suifunite is impossible, since sodium cations form part of the latter. Only K^+ and NH_4^+ were therefore studied in these adsorbents; Na^+ was detected in the first drop of filtrate.

A study of the adsorbability of cations from all groups on bleached clay and talc showed that these adsorbents do not adsorb cations. Cations of the 2nd and 1st groups are not adsorbed on silica gel or chalk either. The cations were detected in the first drop of filtrate.

Experiments were carried out on solutions of pairs of cations at concentrations of 1 N to 0.1 N for each cation.

Because of the strong acidity of solutions of salts of the 5th group cations and of bismuth salts, the adsorption series for these cations could not be established for permutite, bentonite-Askangel, and chalk. When solutions of these salts are brought into contact with the adsorbents, chemical reaction occurs with evolution of gas.

Bentonite-Askangel and bleached clay cannot be recommended for cation separation because they swell considerably in the solutions of the various salts and thereby hinder the passage of the solution through the column.

Adsorption series for anions of all groups on anionite NO are given in Table 2 together with supplementary information on the adsorption of CO_3^{2-} on chromatographic aluminum oxide, of $C_2O_4^{2-}$, CO_3^{2-}, S^{2-}, NO_3^- on anionite MMG-1, and of NO_3^-, $C_2O_4^{2-}$, S^{2-} on anionite TN.

SUMMARY

1. Adsorption series for cations from each analytical group on various adsorbents have been studied: adsorption series for cations of all groups on uifunite Nos. 55, 124, and 127; adsorption series for cations of the 4th and 3rd groups on bentonite-Askangel; adsorption series for cations of the

2nd and 1st on chromatographic aluminum oxide and permutite; and adsorption series for anions of the 1st, 2nd, and 3rd groups on anionite NO.

2. Adsorption series on various adsorbents for each analytical group considered separately have been supplemented for cations of the 5th, 4th, and 3rd group on chromatographic aluminum oxide; for cations of the 4th and 3rd group on permutite; for anions on chromatographic aluminum oxide and the anionites TN and MMG-1.

3. The fact that the experimental results obtained confirm adsorption series obtained previously for anions of the 1st, 2nd and 3rd groups on anionites MMG-1 and TN by coworkers at the Laboratory of the Institute of Physical Chemistry, indicate that these adsorbents are stable.

4. The most suitable adsorbents for each group, whereby developed chromatograms can be prepared are: chromatographic aluminum oxide and Sulfunite Nos., 55, 124 and 127 for cations of the 5th group; chromatographic aluminum oxide, permutite, Sulfunite nos. 55, 124, and 127 for 4th, 3rd and 2nd group cations; chromatographic aluminum oxide and anionite NO for anions of the 1st, 2nd and 3rd groups.

Anionites MMG-1 and TN show poor selectivity for all three groups.

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THE APPLICATION OF PRECIPITATION CHROMATOGRAPHY IN QUALITATIVE SEMI-MICRO ANALYSIS

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Precipitation chromatography, which has been proposed bythe Soviet scientists E. N. Gapon and T. B. Gapon [1], is a variant of M. S. Tsvet's adsorption chromatography, in the successful development of which Soviet scientists have played a leading part.

Precipitation chromatography is based on the separation of materials as precipitates formed on columns filled with carrier and precipitant [2]. The carrier, which is a colorless powdered material, is indifferent to both precipitant and to the test materials. The precipitant is a substance which yields precipitates of different solubilities with the test solutions.

A large number of qualitative reactions for ions are precipitation reactions and can be carried out by different methods. The aim of the present work is the use of precipitation chromatography in qualitative analysis for the detection and separation of particular ions.

As carriers we tried: commercial aluminum oxide for chromatography, silica gel, quartz, asbestos, anionites (anion exchange resins) TN and MMG-1, and cationites (cation exchange resins) MSF and SBS. The best results were given by aluminum oxide and the anionites.

A dry column was used for the detection of Cl^-, Br^-, and I^-, the precipitant being $AgNO_3$ or Ag_2SO_4.

Bi^{3+}, Cu^{2+}, Cd^{2+}, Sn^{2+}, Sb^{3+}, Ag^+, Hg_2^{2+}, Pb^{2+} were detected on a moist column using KI, Na_2S, and $(NH_4)_2S$ as precipitants.

METHOD AND ANALYTICAL PROCEDURE

After a careful investigation of the requisite conditions for getting precipitation chromatograms for qualitative semi-microanalysis, it was found that the best column was a glass tube 4-5 cm long and 3-4 mm in internal diameter. This size of column ensures that the precipitation chromatograms formed are the best possible, and also ensures economy in time and reagents. Only a small amount of the test solution is necessary in order to get a chromatogram.

The dry column was prepared as follows: the carrier is well ground in a porcelain mortar, the precipitant added, and the whole thoroughly mixed. A column with the dimensions given above is fitted with a wad of cotton wool using two glass rods for compacting the wad; the wad is then sprinkled with the mixture of carrier and precipitant. The tube thus filled is connected to a Bunsen flask for filtration under reduced pressure. The column is fixed in a vertical position. A few drops of distilled water are passed through the column, and the charge of carrier packed by dropping tube plus column through another tube, whose internal diameter is big enough and is 1/2 meter in length, 5-10 times until the charge is of uniform density in the column. Whether or not good chromatograms are obtained depends on the even distribution of carrier and precipitant in the column. If the density is not even throughout the charge, the chromatogram will be irregular and diffuse.

Moist columns are prepared by washing the column charged with pure carrier wit a solution of precipitant before preparing the chromatogram.

The charge used in the column is 0.1-0.2 g. The effective length is 1 cm.

The chemicals used were of analytical grade. The concentration of the solutio used were 0.01-0.001 N.

Columns of Al_2O_3 + Precipitant

1. Detection of Cl^-, Br^- and I^- in their mixtures. In order to determine Cl^-, Br^- and I^- in their mixtures we used a dry column. The carrier was Al_2O_3, while the precipitant was either $AgNO_3$ or Ag_2SO_4. Gapon [1], used a ratio of $Al_2O_3:Ag_2SO_4 = 9.1$, i.e., 10% of precipitant. We prepared columns with varying amounts of precipitant. Chromatograms obtained when only 1% of precipitant was used were not inferior to columns containing 10% precipitant.

If a mixture of Cl^-, Br^-, and I^- ions is passed through such a column, a chromatogram is formed in which the zone order from top to bottom is AgI, AgBr, AgCl. The zones are formed in the same order as the respective solubility products:

Solubility product AgI $= 1.5\cdot10^{-16}$
" " AgBr $= 7.7\cdot10^{-13}$
" " AgCl $= 1.56\cdot10^{-10}$

Chromatograms are easily developed in sunlight. Three zones are clearly visible after 5-15 minutes. The first zone is yellow, the second – a bluish gray, while the third is a violet-gray.

On standing, the outward appearance of the chromatograms changes, probably as the result of secondary reactions [2].

It is sufficient to pass only 3 drops of the test solution with concentration varying from 1.0 to 0.0001 N in order to get a well defined chromatogram. The zone length depends on the amount of the particular ion in solution. E.g., on passing three drops of a mixture in which the concentrations of the three ions are 0.1 N, the zone length in each case is 2 mm. We found that the limit of identification for I^- was 8 γ, the limiting concentration being 1:7000, the corresponding values for Cl^- and Br^- were 14-15 γ and 1:4000. In addition we carried out experiments in which the chromatograms of AgI, AgBr, and AgCl were developed with adsorption indicators. On passing an adsorption indicator (e.g. eosin or fluorescein) through the chromatograms all the indicator was held on the upper part of the column and was not distributed evenly through all three zones. On addition of a salt such as Na_2SO_4, the indicator was removed completely from the column. When the indicator was passed through the column as a solution in a buffered acetic acid, it was evenly distributed along all the column, but the zones were not clearly marked. Illumination was essential for final development.

Cl^-, Br^-, and I^- can thus be easily detected by means of precipitation chromatography. Bromine and iodine interfere with the detection of chlorine in the normal methods of qualitative analysis.

2. Detection of Group V Cations. Ag^+, Hg_2^{2+}, Pb^{2+} were detected on a moist column of Al_2O_3 + KI. Attempts to get zones of Ag^+, Hg_2^{2+}, Pb^{2+} on a dry column were unsuccessful.

The chromatograms were developed by passing KI solution through the column. The zone sequence was as follows:

1. Yellow zone of AgI (solubility $1.2 \cdot 10^{-8}$ M/1)
2. Green zone of Hg_2I_2 (solubility $8.8 \cdot 10^{-7}$ M/1)
3. Yellow zone of PbI_2 (solubility $1.2 \cdot 10^{-5}$ M/1) [3].

3. Detection of Certain Elements of the IV Group. Mixtures of Bi^{3+}-Cd^{2+}, Cu^{2+}-Cd^{2+}, Sn^{2+}-Sb^{3+} were detected on a damp Al_2O_3 column using S^{2-} as a precipitant. The precipitant used was a saturated solution of Na_2S or 2.0 N $(NH_4)_2S$, the Al_2O_3 being moistened with the solution. In the case of the mixtures of Bi^{3+}-Cd^{2+}, and of Cu^{2+} and Cd^{2+}, the chromatograms behaved as follows: initially on passing the precipitant through the first time a dark zone of Bi_2S_3 and CuS was formed on top, the next zone was colorless, while the last zone was a yellow CdS zone. On passing the precipitant through the second time the intermediate colorless zone disappeared while the dark zone remained and the yellow zone had shifted up adjacent to it.

When mixtures of Cu^{2+}-Cd^{2+} were chromatographically separated, detection of Cd was rendered difficult in the presence of a large amount of copper because the copper was not completely precipitated in the first zone but passed through all the column and colored it black. The CdS zone was easily distinguishable when the ratio of Cd^{2+} to Cu^{2+} did not exceed 1:4.

Two zones were obtained for mixtures of Sn^{2+}-Sb^{3+}; the upper a brown zone of SnS and the lower an orange one of Sb_2S_3. The drawback of columns using S^{2-} as precipitant is the rapid break-down of the chromatograms by the H_2S evolved by the action of acid solutions of the cations passed through the column. H_2S bubbles fracture the column and thereby destroy the clarity of the zone distribution.

Columns Filled with Synthetic Resins

The anionites (anion exchange resins) TN, MMG-1 and the cationites (cation exchange resins) MSF and SBS were used as carriers. We tried to get a colored chromatogram for mixtures of Cl^-, Br^-, and I^- on a black background using a cationite saturated with Ag^-. We were unsuccessful.

The finely pulverized anionite TN and MMG-1 saturated with I^- gave a precipitation chromatogram for Group V cations in the same way as a column containing $Al_2O_3 + I^-$. Anionites saturated with S^{2-} gave similar precipitation chromatograms to those obtained on $Al_2O_3 + S^{2-}$ columns for mixtures of $Bi^{3+} - Cd^{2+}$, $Cu^{2+} - Cd^{2+}$, $Sn^{2+} - Sb^{3+}$.

The examples given show that precipitation chromatography using our method can be successfully used for qualitative semi-microanalysis. Some of the stages in qualitative analysis can be simplified and shortened by using precipitation chromatography. The methods suggested do not require any special apparatus and can be used in any analytical laboratory.

Further work is required to select suitable carriers and precipitants.

SUMMARY

1. The possibilities of using precipitation chromatography in qualitative semi-microanalysis have been demonstrated.

2. A procedure has been worked out for getting semi-micro chromatograms.

3. Al_2O_3 has been shown to be the most suitable carrier for qualitative precipitation chromatography.

4. A procedure has been developed for the qualitative detection of Cl^-, Br^-, and I^- ions on the basis of a semi-micro precipitation chromatographic method. The sensitivities of the method for these ions has been determined.

5. The possibilities of detecting several cations from their mixtures by a semi-micro precipitation chromatographic method has been demonstrated.

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COMPARATIVE CHARACTERISTICS OF CERTAIN ION-EXCHANGE MATERIALS

Part II

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The close relation between the efficiency of a chromatographic experiment and the nature of the ion-exchange material used necessitates a detailed characterization of the ion-exchange materials used for analytical purposes. In this connection, therefore we adduce in this article supplementary results for materials tested previously, and also results for ion-exchange materials received by the Institute of Geochemistry and Analytical chemistry recently. [1] In both communications the basic characteristics of both cationites (cation-exchange resins) and anionites (anion-exchange resins) which represent practically all ion-exchange materials of Russian origin and the best foreign makes are given.

Physical Properties of Ion-Exchange Materials

Results on the specific gravity of the dry granular material and the relative degree of swelling which were given in our first paper[2] were obtained in accordance with the GOST[3] methods for testing ion-exchange material, which stipulate that all tests should be made on air-dry samples. Nevertheless, in many cases it is of interest to compare the properties of ion-exchange materials of equal moisture contents; as a "standard" the minimum moisture content, which is comparatively easily obtained by drying the test sample to constant weight, is the natural choice. Possible decreases in the exchange capacity which occur to varying extents on drying the samples, cannot, in the given instance, be of particular significance.

In Tables 1-2, results obtained previously for air-dried samples are compared with those for samples dried in a drying oven for 12 hours at 90-100°.

These results show that in the overwhelming majority of cases the specific gravity of the dry granular material determined for the air dried samples and calculated (using a knowledge of the moisture content) from the specific gravity of the dry samples is less than the gravity as determined directly on the dry sample. This is probably explained by the fact that as a consequence of swelling, which is determined by the moisture content of the air-dried sample, the specific gravities of dry ion-exchange materials and materials formerly used in the air-dried state (the amount of moisture in the latter being taken into account) differ among themselves. This assumption, which agrees with differences in the values for relative degree of swelling of air-dried and dried samples, is graphically illustrated in the tables; the relative degree of swelling of air-dried samples in most cases is less than the relative degree of swelling of dried samples. Results which were specially obtained on the relation between relative degree of swelling and moisture content of one of the cationite samples serve as an additional confirmation of the hypothesis advanced above.

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[1] The authors wish to thank representatives of all establishments which sent samples of ion-exchange materials for comparative evaluation.

[2] J. Anal. Chem., No. 3 (1952). (See Consultants Bureau Translation, p. 153.)

[3] All-Union State Standard.

TABLE 1

Cationite tested	Moisture content (%)	Relative degree of swelling, %		Specific gravity of the dry granular material		
		Air-dried	Dried	Air-dried	Calc. on dried	Dried
Espatite-1 (KU-1)	27.1	14	–	0.74	0.54	–
	dried	–	65	–	–	0.86
SBS	26.6	23[1]	–	0.57	0.42	–
	dried	–	54	–	–	0.59
SDV-1	31.0	190	–	0.65	0.45	–
	dried	–	335	–	–	0.69
SDV-2	17.2	135	–	0.50	0.42	–
	dried	–	166	–	–	0.49
KN	4.8	25	–	0.40	0.21	–
	dried	–	16	–	–	0.43
KM	16.3	108	–	0.48	0.40	–
	dried	–	89	–	–	0.50
Sulfonated coal	15.0	33	–	0.67	0.57	–
	dried	–	44	–	–	0.64

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[1] In our first paper a value of zero was given for the degree of swelling; this apparently related to a sample of high moisture content.

TABLE 2

Anionite tested	Moisture content (%)	Relative degree of swelling, %		Specific gravity of the dry granular material		
		Air-dried	Dried	Air-dried	Calc. on dried	Dried
MN	10.7	40	–	0.63	0.56	–
	dried	–	47	–	–	0.65
TN	18.8	1	–	0.34	0.28	–
	dried	–	19	–	–	0.34
N-O	12.9	23	–	0.25	0.20	–
	dried	–	39	–	–	0.40
MMG-1	9.2	24	–	0.80	0.73	–
	dried	–	44	–	–	0.86
N	12.7	21	–	0.52	0.45	–
	dried	–	35	–	–	0.54
VS	14.1	27	–	0.34	0.29	–
	dried	–	42	–	–	0.36
TM	9.6	12	–	0.80	0.72	–
	dried	–	20	–	–	0.93

Moisture content	16.8	17.4	23.5	27.0	36.4
Relative degree of swelling	100	77	60	50	33

In accordance with the results obtained, the relative degree of swelling and the specific gravity of the dry granular material of the new test ion-exchange materials were determined on the dried samples. The respective results are given in Table 3.

TABLE 3

Cationite tested	Relative degree of swelling (%)	Specific gravity of granular material	Anionite tested	Relative degree of swelling (%)	Specific gravity of granular material
KU-2	108	0.80	AN-1F	37	0.57
KB-4	33	0.72	AN-2F	29	0.55
SBSR	50	0.66	AN-4K	8	0.35
SM-12	370	0.67	AN-7K	33	0.42
RF	93	0.74	PE-9	96	0.55
			EDE-10	127	0.54

TABLE 4

Cationite				Anionite			
Sample tested	Moisture content (%)	Relative degree of swelling, %		Sample tested	Moisture content (%)	Relative degree of swelling, %	
		water	1 N KCl			water	1 N KCl
KU-2	18.0	36	22	AN-1F	7.5	50	44
KB-4	7.5	38	42	AN-2F	8.8	47	59
SBSR	8.3	52	44	AN-4K	33.0	14	7
SM-12	13.6	258	148	AN-7K	13.2	54	34
RF	8.7	62	57	PE-9	7.6	117	87
				EDE-10	6.6	106	88

TABLE 5

Cationite tested	Total exchange capacity at pH of			
	3	5	7	13
Espatite-1 (KU-1)	2.6	2.75	2.88	6.02
SBS	3.08	3.29	3.43	4.80
SDV-1	5.8	6.1	6.22	6.22
SDV-2	4.7	4.82	4.95	4.82
KN	0	0.126	0.37	2.95
KM	0.18	1.19	3.22	11.20
Sulfonated coal	1.18	1.77	2.0	4.24
KU-2	4.7	4.7	4.75	5.02
KB-4	0.16	1.08	4.3	8.55
SBSR 1)	1.68	1.85	1.96	2.75
SM-12	3.25	3.45	3.65	4.85
RF	3.03	3.8	4.4	6.98

1) According to the makers of this resin, the sample tested has a low exchange capacity in comparison with the majority of batches of this cationite.

TABLE 6

Anionite tested	Total exchange capacity at pH of	
	7	1
MN	1.97	4.6
TN	0.93	3.95
N-O	1.42	4.49
MMG-1	2.42	4.61
N	2.02	5.06
VS	0.23	3.96
TM	0.28	4.45
AN-1F	0.90	7.28
AN-2F	1.92	8.4
AN-2K	1.72	6.1
AN-4K	1.84	7.47
PE-9	0.84	5.3
EDE-10	1.51	7.79

Just as for samples tested previously, an appreciable difference was observed between the values of the relative degree of swelling in water and in KCl solutions. The results are given in Table 4.

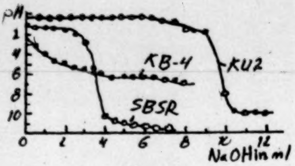

Fig. 1.

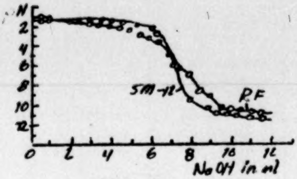

Fig. 2.

Exchange Properties

As indicated in our first paper the most important index of the exchange properties of cationites and anionites for chromatographic practice is the exchange capacity at the pH's determined by the nature of the test mixtures. The samples have been tested again and the curves given in Figs. 1-5 are the results of potentiometric titrations; as before these curves were taken by the method of individual aliquots. Values for the total exchange capacity of the various cationites at pH's of 3,5,7 and 13, respectively, are given in Table 5; the first three values are taken from the potentiometric curves, while the rest were determined by leaving an aliquot in 0.1 N NaOH and subsequent titration of excess unreacted alkali. Values of the exchange capacity of anionites at pH 7 (according to the potentiometric titration curve) and pH 1(according to back titration of the unreacted acid) are given in Table 6. For comparison, the exchange capacity of ion-exchange materials of Russian manufacture examined previously are included in the tables as well. In all cases the capacity is expressed as mg. equivalents/g of dry material.

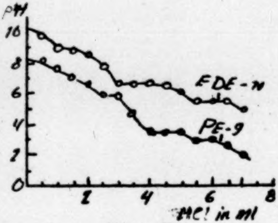

Fig. 3.

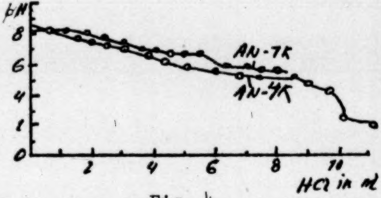

Fig. 4.

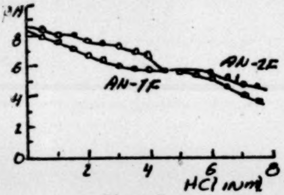

Fig. 5.

A comparative study of a large number of cationites and anionites leads us to conclude that the best ones for chromatographic analysis are the cationites KU-2, SBS, KB-4 and the anionites MMG-1, PE-9, EDE-10 and AN-2F.

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A NEW, QUALITATIVE REACTION FOR THIOCYANATES

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Some of the characteristic qualitative reactions which have been used for the detection of thiocyanates are; the formation of dark red ferric thiocyanate $Fe(CNS)_3$ [1], the formation of the dark blue complex of cobalt $(NH_4)_2[Co(CNS)_4]$ [2]; the formation of the green pyridine thiocyanate complex of copper $CuPy(CNS)_2$ [3]; the formation of canarinic ($C_4H_4N_8S_7O$) and pseudothiocyanic ($HC_3N_3S_3$) acids, with a characteristic bright yellow color [4]; the formation of molybdenum thiocyanate, which has an intense orange yellow color [5]; and finally the catalytic acceleration of the iodazide reaction by thiocyanates [6], and other reactions.

The reaction between trivalent iron and thiocyanates for the determination of the latter is not applicable when acetates and iodides are present, since they form red-brown solutions with trivalent iron.

We propose a new color reaction for thiocyanates, by means of which they can be detected in the presence of acetates and iodides. This reaction is based on the formation of a characteristic yellow brown precipitate which is formed on interaction of thiocyanates with an acetic acid solution of a salt of bivalent copper with aniline.

I. M. Korenman has suggested a reaction for detecting cupric ions based on the formation of a crystalline precipitate corresponding to the formula $[Cu(C_6H_5NH_2)\cdot 5H_2O](CNS)_2$ by the use of aniline hydrochloride in conjunction with a saturated solution of ammonium thiocyanate [7].

We have shown that soluble salts of the complex cation $[Cu(C_6H_5NH_2)\cdot 5H_2O]^{2+}$ can be used for detecting thiocyanate ions in the presence of acetates and iodides.

The reaction proceeds as follows:

$$[Cu(C_6H_5NH_2)\cdot 5H_2O](C_2H_3O_2)_2 + 2NH_4CNS = [Cu(C_6H_5NH_2)\cdot 5H_2O](CNS)_2 + 2NH_4C_2H_3O_2.$$

A similar reaction occurs when o- and p-toluidine are used.

EXPERIMENTAL

The reaction can be carried out in a test tube, on a spot test plate, on filter paper, and also microcrystalloscopically.

To 1 ml reagent is added 1 ml of the neutral test solution. A yellow-brown crystalline precipitate is formed in the presence of thiocyanate. Precipitate separates out of dilute solution after 1-2 minutes. A drop of reagent and a drop of test solution are placed on a spot test plate. A yellow brown precipitate is formed.

A drop of reagent and a drop of test solution are placed on a filter paper. A yellow-brown spot forms if thiocyanate is present. At low thiocyanate concentrations the color may not be very distinct. In such a case the paper is washed with distilled water. All soluble salts are washed out, while the precipitate will be retained by the filter pores. A drop of ferric chloride is placed on the dark spot of precipitate. If thiocyanates are present a red spot will be formed. The sensitivity of the reacti is 20γ.

For microcrystalloscopic detection the drop of reagent plus a drop of test solution are placed on the microscope object slide. Characteristic golden crystals are observed. The sensitivity in this case is 1γ.

TABLE 1

The effect of acetic acid concentration

Acetic acid conc. in %	Time for ppt. to form
5	0.5 min.
10	1 min.
25	1 min.
50	No. ppt.

TABLE 2

The effect of aniline concentration

Aniline conc.,%	Time for ppt. to form
1	1 min.
3	30 sec.
5	10 sec.

Examination of the precipitate showed the presence of cupric ions, thiocyanate ions and aniline. Cupric ions were shown to be present by the formation of the cuprammonium complex, the thiocyanate ions by reaction with ferric iron, and aniline by the formation of oxidation products on reacting with calcium hypochlorite. The precipitate dissolved readily in 2 N HCl and HNO_3 with the formation of yellow solutions. In order to find out the optimum conditions for carrying out the reaction, a series of experiments were carried out. The results are given in Tables 1, 2 and 3.

TABLE 3

Effect of the ratio of cupric acetate solution to aniline

5% solution of aniline in 5% acetic acid, in ml.	0.1 N cupric acetate, in ml	Time for ppt. to form
2	1	1 min.
1	1	10 sec.
1	2	10 sec.
1	3	1 min.

TABLE 4

Determination of the reaction sensitivity in a test tube (1 ml of ammonium thiocyanate and 1 ml reagent)

Conc. of CNS^- in mg/ml	Effect of the reaction
10	Bulky yellow-brown ppt.
1	Yellow-brown ppt. after 15 sec.
0.5	Small ppt. after 3 min.
0.3	No ppt. formed.

In order to determine the influence of acetic acid concentration on the sensitivity of the reactions, the following solutions were prepared: a 10% aniline solution, 0.1 N cupric acetate, a solution of ammonium thiocyanate corresponding to a thiocyanate concentration of 1 mg/ml, and acetic acid solutions of various concentrations. The volume of each component used for the reaction was 1 ml.

In order to choose the aniline concentration, the following solutions were used: 0.1 N cupric acetate, a solution of ammonium thiocyanate equivalent to 1 mg thiocyanate/ml, solutions of aniline of various concentration in 5% acetic acid. The volume of each component was 1 ml.

It was found that the reaction was most sensitive when the reagent employed consisted of a 5% solution of aniline in 5% acetic acid plus 0.1 N cupric acetate solution used in the ratio of 1:1 or 1:2. The pH was 4.5-5.

The reagent was prepared as follows: 5 g of freshly distilled aniline (b.p. 184.4°) was dissolved on heating in 95 ml of 5% acetic acid. A solution of 0.1 N cupric acetate was then added to the transparent solutions thus obtained in the ratio 1:1. The solution is green. On storing, the reagent decomposes.

TABLE 5

Sensitivity of the reaction when carried out as a microcrystalloscopic reaction (1 drop of ammonium thiocyanate and 1 drop of reagent)

Conc. of CNS^-, in mg/ml	Appearance of ppt.	Character of the crystals
1	Immediately.	The field of vision is filled with golden crystals in the form of rectangles and crosses.
	After 5 min.	Long golden needles in the form of bundles and branches form along the edges.
0.5	Immediately	Many golden crystals in the form of rectangles and crosses.
	After 5 min.	Long golden needles in the form of bundles and branches form along the edges.
0.1	After 10 min.	Individual golden crystals in the form of rectangles, trapeziums and crosses.
0.05	After 10 min.	Individual golden crystals in the form of rectangles and crosses.
0.03	After 15 min.	1-2 crystals in the form of rectangles.
0.01	Ditto	No crystals formed.

It is recommended therefore that the aniline and cupric acetate solutions should only be mixed prior to use. A number of experiments were carried out to determine the sensitivity. The results are given in Tables 4 and 5.

0.5 mg/ml of thiocyanate can be detected if the reaction is carried out in a test tube. Limiting concentration 1:4000.

The sensitivity of the microcrystalloscopic variant is 1γ. The sensitivity is 20γ when carried out on filter paper. Ferro- and ferricyanides and sulfides must be removed first by precipitation with zinc acetate before testing for thiocyanates by this method; nitrite ions destroy the sulfamic acid.

SUMMARY

1. A new reaction is suggested for thiocyanate detection. It has been established that when thiocyanates react with an acetic acid solution of the salt formed between cupric copper and aniline, a yellow-brown precipitate is formed.

2. The reaction is sensitive enough to be used both as a spot test and as a microcrystalloscopic reaction.

3. Thiocyanates can be detected in the presence of acetates and halides by means of this reaction.

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AN EMPIRICAL SERIES OF SOLUBILITIES FOR THE FERROCYANIDES

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A knowledge of the comparative solubilities of difficultly soluble electrolytes is of great theoretical and practical significance [1-5].

Hydroxides or salts with the same anions or cations can be arranged in order of decreasing or increasing solubility. In addition to the hydroxides [1], there are also such series for sulfides [1,2,4], metavanadates [3], oxalates, sulfates, chromates, and salts of lead and silver [2].

Our aim was to establish an empirical series of solubility for heavy metal ferrocyanides.

The ferrocyanide ion forms practically insoluble salts with the majority of the heavy metal ions, which fact is a valuable property from the viewpoint of the chemical technologist and analyst.

We only managed to find the following results on ferrocyanide solubilities in the literature.

$K_2Zn_3[Fe(CN)_6]_2$	$9.91 \cdot 10^{-3}$ g/l	$1.42 \cdot 10^{-5}$ mol/l	[6]
$K_2Mn[Fe(CN)_6]$	$6.72 \cdot 10^{-2}$ "	$1.95 \cdot 10^{-4}$ "	[6]
$Pb_2[Fe(CN)_6] \cdot 3H_2O$	$1.09 \cdot 10^{-2}$ "	$1.75 \cdot 10^{-5}$ "	[6]
$Ag_4[Fe(CN)_6] \cdot H_2O$	"	$2.27 \cdot 10^{-9}$ "	[7] Sp (activity product 0.01-0.1 M) = $2.27 \cdot 10^{-4}$ [9] and $1.3 \cdot 10^{-9}$ mol/l, Lp = $1.3 \cdot 10^{-42}$ [8]

$Ag_4[Fe(CN)_6]$: $2.2 \cdot 10^{-9}$ and Sp = $1.5 \cdot 10^{-41}$

$Ba_2[Fe(CN)_6] \cdot 6H_2O$ 1 part at 15° soluble in 1000 parts H_2O [10-14]

1 " 75° " 100 "

When the following ions are also present in solution we get [19]:

Ag^+ and Cu^{2+}	the ferrocyanide	precipitates	first the	Ag^+	ions,
Zn^{2+} and Cu^{2+}	"	"	"	Zn^{2+}	"
Co^{2+} and Zn^{2+}	"	"	"	Zn^{2+}	"
Fe^{2+} and Zn^{2+}	"	"	"	Zn^{2+}	"
Co^{2+} and Mn^{2+}	"	"	"	Mn^{2+}	"
Fe^{4+} and Ag^+	"	"	"	Ag^+	"

Before the Ag^+ ions precipitate qualitatively Fe^{3+} starts to precipitate.

One of the reasons for the paucity of information on ferrocyanide solubility as pointed out by Mozander [16] and Williamson [17], is the relation between the composition of the precipitates and the conditions under which they have been precipitated, and their tendency to form double or ternary salts [19]. According to Tananaev and Levina [15], precipitates of simple ferrocyanides of the type $Me_2^{II}[Fe(CN)_6]$, are formed comparatively rarely, e.g., on reaction with $H_4[Fe(CN)_6]$, $Li_4[Fe(CN)_6]$, and partly with $Na_4[Fe(CN)_6]$.

In the case of nickel salts they showed that in the majority of cases, e.g., with $K_4Fe(CN)_6$, the reaction proceeds in three stages; first a simple ferrocyanide is formed, then (according to the increase in alkali metal concentration) solid solution, and finally double salts.

According to Rene Paris [18], who confirmed Wyroubow's opinion [11], the composition of the precipitates also depends on the order in which the reagents are mixed.

From what has been said it is obvious that determinations of the absolute values for the solubilities of the ferrocyanides are accompanied by great difficulties, and that even if these difficulties should be overcome and a solubility series established, then the latter might turn out to be of no practical significance, since $K_4Fe(CN)_6$ which is almost exclusively used for the preparation of ferrocyanides, has been shown to give ferrocyanide precipitates of variable composition.

In order, therefore, to solve the problem specified, i.e. establishing a "practical" series for the solubilities of ferrocyanide precipitates, we studied precipitates obtained under certain definite experimental conditions viz; precipitates obtained by the action of $K_4Fe(CN)_6$ in neutral or weak salt, or weak acid media (up to 0.5 N) in the presence of a large excess of precipitant (in the form of a solid phase).

EXPERIMENTAL

It is assumed that the cation which gives the least soluble ferrocyanide will drive out ("substitute") another cation from the precipitate of a more soluble ferrocyanide. Experiments were carried out in the cold and on heating (duplicate) in the presence of excess liquid or solid phase. After equilibrium has been reached both phases were qualitatively analyzed for the presence of metal cation or ferrocyanide anions.

When this was done it was observed that the following stages could be obtained:

complete substitution
considerable "
little "
no substitution

Because the arrangement of the ferrocyanides of Co^{2+}, Ni^{2+}, Pb^{2+}, Mn^{2+} in a solubility series could not be determined by one method (the results were not reproducible), we were compelled to use several methods.

First Method. A suspension of freshly prepared and carefully water-washed precipitate of the ferrocyanide of each of the metals indicated below was added in large excess (visually) with respect to the amount of it required for precipitation of a given ion, to 10-15 ml of 0.1 N solution of the nitrate (or sulfate) of the test metal and the mixture shaken for 5 minutes in the cold.

In a parallel experiment the contents of the test tube were boiled for 5 minutes. The precipitate was then filtered and washed with water. The filtrate and precipitate were then tested with special reagents for the presence or absence of the cation being studied.

Second Method. To 15 ml of a 0.1 N solution of the metal salt was added a solution of potassium ferrocyanide in an amount insufficient for complete precipitation of the test cation.

To the solution and precipitate thus prepared was added 1 ml of a 0.1 N solution of the salt of another metal and the mixture heated to the boil. The precipitate was filtered off and the presence of the cation of the other metal tested for in the filtrate by a special reagent.

Third Method. A mixture of equal amounts (2 ml) of 0.1 N solutions of the mixture of two metals[1] was prepared and a 0.1 N solution of potassium ferrocyanide added in an amount insufficient for complete precipitation of both cations of the mixture and the whole brought to the boil. The precipitate formed was filtered off and the presence of the two cations tested for in the filtrate by special reactions. When both cations were found in the filtrate the amount of precipitant used was increased. Experiments were repeated until the only cation to remain in solution in the filtrate was the one which formed the most soluble ferrocyanide.

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[1] Bivalent iron was used as the sulfate.

Fourth Method. The precipitates obtained on addition of the first drop of ferrocyanide were examined.

The various methods used agreed well among themselves.

The solubility of the metal ferrocyanides decreases in the following sequence[1]:

$$Pb^{2+} > Al^{3+} > Bi^{3+} > Sb^{3+} > Mn^{2+} > Cd^{2+} > Co^{2+} > Ni^{2+} > Fe^{2+} > Zn^{2+} > Fe^{3+} > Cu^{2+} > Ag^{+}$$

The only exception which we found to the general rule that metals displaced cations standing to the left of them in the series from their ferrocyanides was lead.

Although in the case of lead all the cations which we tested displaced Pb^{2+} from its ferrocyanide, nevertheless Pb^{2+} was precipitated to a considerable extent by cobalt ferrocyanide. We consider that this fact does not discredit the series we established. According to our observations only the formation of silver ferrocyanide is practically irreversible; in the other cases the direction of the interaction between the pairs of components which we used depends on the concentration of the cation in the solution standing over the precipitate. N. A. Tananaev came to the same conclusion when comparing the solubilities of hydroxides [1].

On the basis of this series we worked out a satisfactory method for the purification of nickel ferrocyanides in the nickel liquors from the Pyshminsky Electrolytic Factory from impurities.

Examples of the application of the solubility series of the ferrocyanides are the methods which have been developed for 1) detection of cadmium in the presence of copper, and 2) detection of aluminum in a mixture of all the cations[2].

SUMMARY

An empirical series for the solubility of metal ferrocyanides has been established.

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Our observations indicate that Sb^{3+} does not oxidize $[Fe(CN)_6]^{4-}$.

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METHODS FOR THE ANALYSIS OF SIMPLE HALOGENATED ETHERS

THE ANALYSIS OF α-HALOGENO-DIALKYL AND α-ETHYLARYL ETHERS

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α-Halogeno-dialkyl and ethylaryl ethers of the general formula

$$R-CH_2CHHal-OR', \text{ where } R = H, CH_3; Hal = Cl, Br; R' = Alk, Ar$$

are prepared at present by hydrohalogenation of the simple vinyl ethers, a method worked out by the authors:

$$CH_2{=}CH-OR + HHal \longrightarrow CH_3-CH\cdot Hal-OR$$ [1,2].

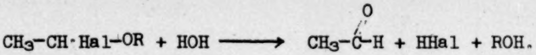
This simple method of synthesizing α-halogeno ethers gives a quantitative yield and the synthesis is not accompanied by side reactions, so that the products can be used in many cases for further synthesis without distillation. α-Halogeno-dialkyl and ethylaryl ethers are extremely reactive compounds. Their tendency to react chemically is manifested in condensation reactions [3,4,5], and in the substitution of chlorine by bromine [1,6],

$$CH_3-CHCl-OAlk + Br_2 \longrightarrow CH_2Br-CHBr-OAlk + HCl; \; CH_3-CHCl-OAlk + HBr \longrightarrow$$

$$\longrightarrow CH_3-CHBr-OAlk + HCl,$$

in their instability to light, heat and moisture. The reactivity of α-halogeno ethers is particularly clearly demonstrated by their hydrolytic breakdown. Even atmospheric moisture causes these compounds to fume with evolution of the hydrogen halides.

Their hydrolysis in excess water at room temperature is instantaneous, and as a result acetaldehyde, hydrogen halide and the respective alcohol are formed.



$$CH_3-CH\cdot Hal-OR + HOH \longrightarrow CH_3-\overset{O}{\overset{/\!/}{C}}-H + HHal + ROH.$$

TABLE 1

Constants of the α-halogeno-ethers analyzed

Formula of the ether	Boiling point (°C) (pressure in mm Hg)	n_D^{20}	d_4^{20}
$CH_3-CHCl-OCH_3$	69.5-70/760	1.3960	1.0003
$CH_3-CHCl-OC_2H_5$	28-29/57	1.4021	0.9495
$CH_3-CHCl-OC_4H_9$	34-35/7	1.4126	0.9339
$CH_3-CHCl-OC_6H_5$	97-98/24	1.5225	1.1150
$CH_3-CHBr-OCH_3$	56.5-57/158	1.4486	1.4253
$CH_3-CHBr-OC_2H_5$	40-41/42	1.4465	1.2770
$CH_3-CHBr-OC_4H_9$	57-58/10	1.4485	1.2086
$CH_3-CHBr-OC_6H_5$	88-89/7	1.5500	1.3640
$CH_2Cl-OC_4H_9$	55-56/48	1.4208	0.9665

The rate of hydrolysis of the halogeno ethers is similar to that of ionic reactions, so that all the members of this group can be quantitatively titrated with 0.1 N NaOH using methyl orange as an indicator, while the halide can be titrated with 0.1 N $AgNO_3$, and the acetaldehyde by the bisulfite method.

This property of the halogeno ethers was used for their qualitative and quantitative determination. The rate of hydrolysis of halogeno ethers in excess

TABLE 2

Formula of the ether	Weight, in g	0.1 N NaOH used, in ml	Molecular weight		α-Halogeno ether, %
			Found	Calculated	
$CH_3-CHCl-OCH_3$	0.1841	19.30	95.30	94.54	101.02
	0.2388	24.93	95.78		101.30
$CH_3-CHCl-OC_2H_5$	0.1814	16.27	111.5	108.57	102.6
	0.1750	15.77	111.0		102.2
$CH_3-CHCl-OC_4H_9$	0.2536	18.57	136.50	136.62	99.93
	0.1968	14.41	136.52		99.93
$CH_3-CHCl-OC_6H_5$	0.2750	17.37	158.31	156.61	101.1
	0.2516	16.01	157.10		100.3
$CH_3-CHBr-OCH_3$	0.1261	8.91	141.54	139.00	101.8
	0.1379	9.78	141.01		101.5
$CH_3-CHBr-OC_2H_5$	0.3311	20.99	157.7	53.03	103.0
	0.3208	20.57	155.9		101.9
$CH_3-CHBr-OC_4H_9$	0.1467	8.02	182.91	181.08	101.0
	0.1464	7.97	183.68		101.4
$CH_3-CHBr-OC_6H_5$	0.1672	8.25	202.6	201.07	100.75
	0.1428	7.03	203.2		101.05
$CH_2Cl-OC_4H_9$	0.2200	17.98	122.37	122.60	99.84
	0.2084	16.97	122.80		100.20

TABLE 3

Formula of the ether	Weight, in g	0.1 N $AgNO_3$ used, in ml	Halogen, in %		α-Halogen ether, %
			Found	Calculated	
$CH_3-CHCl-OCH_3$	0.1480	15.27	36.50	37.51	97.31
	0.1628	16.97	36.96		98.53
$CH_3-CHCl-OC_2H_5$	0.1900	16.97	31.67	32.65	97.00
	0.1870	16.73	31.72		97.15
$CH_3-CHCl-OC_4H_9$	0.1815	13.127	25.62	25.96	98.69
	0.2009	14.267	25.19		97.04
$CH_3-CHCl-OC_6H_5$	0.1520	9.62	22.44	22.65	99.07
	0.1493	9.38	22.30		98.45
$CH_3-CHBr-OCH_3$	0.1360	9.77	57.40	57.50	99.83
	0.1566	11.25	57.40		99.83
$CH_3-CHBr-OC_2H_5$	0.3200	20.58	51.40	52.24	98.39
	0.3108	20.35	52.33		100.1
$CH_3-CHBr-OC_4H_9$	0.1664	9.04	43.42	44.13	98.39
	0.1853	10.12	43.65		98.91
$CH_3-CHBr-OC_6H_5$	0.1400	6.90	39.38	39.74	99.10
	0.1532	7.60	39.64		99.75
$CH_2Cl-OC_4H_9$	0.1736	13.62	27.82	28.92	96.20
	0.1686	13.32	28.01		96.85

TABLE 4

Formula of the ether	Weight, in g	0.1 N I_2 used, in ml	CH_3CHO/1 mol ether, in g		α-Halogeno ether, %
			Found	Calculated	
$CH_3-CHCl-OC_2H_5$	0.0892	16.30	43.66	44.05	99.23
	0.0902	16.45	43.57		99.02
$CH_3-CHCl-OC_4H_9$	0.0910	13.30	43.93	44.05	99.84
	0.1100	16.08	43.94		99.86
$CH_3-CHCl-OC_6H_5$	0.1658	21.07	43.80	44.05	99.55
	0.1726	22.01	43.92		99.82
$CH_3-CHBr-OC_4H_9$	0.1210	13.07	43.07	44.05	97.89
	0.1198	13.00	43.27		98.34
$CH_2Cl-OC_4H_9$	0.1945	31.77	29.76	30.02	99.20
	0.1864	29.79	29.39		97.97

water under the conditions employed is practically independent of the molecular weight of the radical linked directly to oxygen. There is practically no difference either in the hydrolysis of α-halogeno methyl and α-halogenoethylalkyl ethers of the formulas;

$$CH_2Hal-OR \text{ and } CH_3-CHHal-OR.$$

The Qualitative Reactions used for α-Halogeno Ethers Were; 1) with fuchsin sulfurous acid (Schiff's reagent) a red color develops which changes into the violet characteristic of aldehydes; 2) with a solution of $AgNO_3$ a white precipitate of AgCl is formed; 3) a red color develops with methyl orange in aqueous media.

TABLE 5[1]

Formula of the ether	Halogen found by combustion, %	Halogen found by titration with 0.1 $AgNO_3$, %	Halogen calculated, %
$CH_3-CHCl-OCH_3$	37.02	36.73	37.51
$CH_3-CHCl-OC_6H_5$	22.55	22.37	22.65
$CH_3-CHBr-OCH_3$	57.56	57.40	57.50

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[1] The average of 2 duplicates is given in the table.

α-Halogeno Ethers can be Determined Quantitatively by three methods: 1) titration of free acid with 0.1 N NaOH (Table 2); 2) titration of free Cl^- with 0.1 N $AgNO_3$ (Table 3); and 3) titration of free aldehyde with bisulfite (Table 4).

All three methods give good agreement (Table 5) among themselves and with the results of halide determinations by the combustion method (Table 6).

The methods enumerated were tested on 8 representative of the α-halogeno ethers synthesized by the methods described above [1,2].

EXPERIMENTAL

The ethers analyzed had the constants given in Table 1 (constants of the α-halogeno ethers analyzed).

TABLE 6

Formula of the α-halogeno ether	By titration with 0.1 N NaOH	By titration with 0.1 N $AgNO_3$	By titration with bisulfite	Halogen by combustion
$CH_3-CHCl-OC_6H_5$	101.1 100.3	99.07 98.45	99.55 99.82	99.03 100.05
$CH_3-CHCl-OCH_3$	101.02 101.30	98.09 99.33	- -	98.15 99.25
$CH_3-CHBr-OCH_3$	101.80 101.50	99.83 99.83	- -	99.55 100.65
$CH_3-CHBr-OC_4H_9$	101.00 101.40	98.39 98.91	97.89 98.34	- -

1. The Quantitative Determination of Halogen in α-Halogeno Ethers by Titration with 0.1 N NaOH.

An ampoule containing the test ether was placed in a flask with a ground glass stopper and containing 25 ml distilled water. The ampoule was broken and the liquids carefully mixed and then titrated with 0.1 N NaOH using methyl orange as indicator.

2. The Quantitative Determination of Halogen in α-Halogeno Ethers by Titration with 0.1 N $AgNO_3$.

25 ml of 0.1 N $AgNO_3$, 20 ml of distilled water and an ampoule of the test ether were placed in a ground glass stoppered flask. The ampoule was broken, the liquids mixed and then excess $AgNO_3$ back titrated with 0.1 N KCNS using ferric alum as indicator.

3. The Quantitative Determination of Acetaldehyde in α-Halogeno Ethers by the Bisulfite Method.

20 ml of distilled water, 25 ml of 0.2 N sodium bisulfite and an aliquot of the test ether were placed in a ground glass stoppered flask. The liquids were well mixed for 15 minutes and after a further 15 minutes standing the excess bisulfite was back titrated with 0.1 N iodine. Blank tests were made in each instance.

Results for the analysis of 9 halogeno ethers are given in Tables 2, 3, 4, 5 and 6. Only one of the many replicate results are given for each ether.

SUMMARY

1. Methods are described for the determination of the concentration of α-halogeno ethers, which are based on the rapid hydrolysis of these compounds.

2. The methods proposed enable the amount of functional halogen, the concentration of α-halogeno ether, the position of the halogen and the composition of the alkyl radical to be determined; they can also be applied for mixtures of the halogenated ethers with neutral solvent.

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1) See Consultants Bureau Translation, pp. 1367, 2) ibid, pp. 329 ff.

THE USE OF THE LUNGE NITROMETER FOR THE DETERMINATION OF NITROSAMINES, NITRAMINES, AND ALKYL NITRATES

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Quantitative reduction of nitric and nitrous acids, their salts and certain of their derivatives by mercury in sulfuric acid media to give nitric oxide is used in organic analysis mainly for the gas-volumetric determination of nitrocellulose and nitroglycerol. References in the literature [1, 2, 3], to the possibility of using this reaction for analyzing other organic derivatives of nitric and nitrous acid are very meager.

The results of our observations on the applicability of reduction in a nitrometer for the determination of the simplest esters of nitric acid, N-nitroso and N-nitro groups are given in the present paper, in addition to observations on the possibility of determining nitric acid in the presence of certain organic compounds by this method.

Experiments, the results of which are given below were carried out in a standard five-limbed nitrometer by the usual method used for nitrocellulose analysis. Preparations of dialkyl-nitrosamines were made by distillation of the hydrochlorides of the respective amines with sodium nitrite [4], while dicyclohexylnitrosamine was made by heating dicyclohexylamine acetate with sodium nitrite [5]. Dimethylnitramine was prepared by dehydration of dimethylamine nitrate with acetic anhydride [6], while methyl and ethyl nitrates were made by the action of nitric acid on the respective alcohols [7]. Dialkyl-nitrosamines and alkyl nitrates were purified by distillation, while dicyclohexylnitrosamine and dimethylnitramine were purified by recrystallization. The constants for these preparations were in good agreement with published results. The nitric acid used was chemically pure grade, sp. gr. 1.4.

Cope and Barab [1] recommended a nitrometric method for the determination of nitro groups in N-nitramines, and of nitroso groups in N-nitrosamines. These authors reckoned that the capacity to be reduced by mercury in sulfuric acid is characteristic of nitramines and nitrosamines, which clearly distinguishes them from C-nitro and C-nitroso compounds. Cope and Barab came to this conclusion on the basis of experiments with nitro-urea, nitro-guanidine, tetryl, and diphenylnitrosamine. In attempting to use the Lunge nitrometer for the determination of aliphatic and alicyclic nitrosamines and nitramines we found that dimethyl-, diethyl-, di-n-propyl- and dicyclohexyl nitrosamines and also dimethyl nitramine, in general did not evolve gas on shaking with concentrated sulfuric acid and mercury at room temperature. These compounds, therefore, while being typical representatives of the nitrosamines and nitramines, differ sharply from nitro-urea, nitroguanidine, and their aromatic analogs in their behavior in a nitrometer. Thus, despite what the American authors say [1], the capacity to be reduced in a nitrometer cannot be regarded as characteristic of the group $>N{-}NO_2$ and $>N{-}NO$ as distinct from $\equiv C{-}NO_2$ and $\equiv C{-}NO$ and the results which they obtained must be regarded as a consequence of the effect of the $>C{=}O$ group connected to nitrogen (in nitro-urea), of $>C{=}NH$ (in nitro-guanidine) and of the benzene ring (in tetryl and diphenyl nitrosamine).

TABLE 1

Determination of the lower alkyl nitrates in a nitrometer

Test substance	Amount taken, in mg	Amount found, in mg	Difference, %
Methyl-nitrate (17.4% solution in acetic acid). . .	112.3	115.0	+ 2.4
Methyl-nitrate (17.4% solution in acetic acid). . .	141.6	143.8	+ 1.6
Methyl-nitrate (15.2% solution in methyl alcohol) .	70.2	68.5	- 2.4
Methyl-nitrate(15.2% solution in methyl alcohol) .	72.5	70.2	- 3.2
Ethyl-nitrate	186.4	98.1	-47.3
Ethyl-nitrate	172.2	83.3	-51.7
Ethyl-nitrate.	370.8	199.5	-46.2
Ethyl-nitrate (75% solution in ethyl alcohol)	133.6	117.0	-12.4
Ethyl-nitrate (80% solution in ethyl alcohol)	198.6	75.6	-60.9

TABLE 2

Determination of nitric acid in a nitrometer in the presence of organic compounds

Organic compounds	Taken		Found	
	Organic compound, in mg	HNO_3, in mg	HNO_3, in mg	% of the acid found
Methyl alcohol	449	301.1	304.2	101.0
Methyl alcohol	1848	271.9	267.3	98.3
Ethyl alcohol	535	214.5	131.7	61.5
Ethyl alcohol	1374	328.4	165.2	50.3
Isopropyl alcohol . .	678	368.9	299.7	81.2
Isopropyl alcohol . .	1213	234.5	184.9	78.8
Isobutyl alcohol . . .	848	227.6	64.2	28.2
Isobutyl alcohol . . .	2383	287.1	18.0	6.3
Dimethylnitrosamine. .	381	58.1	58.0	99.8
Dimethylnitrosamine. .	621	94.7	94.3	99.6
Diethylnitrosamine . .	187	154.7	155.6	100.6
Diethylnitrosamine . .	259	79.6	79.6	100.0

We also checked on the possibility of using the nitrometric method for the analysis of simple alkyl nitrates. The results obtained (some of which are published in Table 1) show that methyl nitrate can be determined with a fair degree of accuracy (up to 2-3% of the amount taken), while the method is not suitable for the determination of ethyl nitrate; the results in the latter case being low and variable. In the case of ethyl nitrate, reduction to nitric oxide is presumably accompanied by other processes and leads to the formation of nitrate compounds which cannot be reduced to nitric oxide.

The results given in Table 2 are for the determination of nitric acid in the presence of a number of alcohols and aliphatic nitrosamines. In these experiments the aliquots of nitric acid and the organic compound are mixed in the nitrometer funnel directly before determination.

These results show that methyl alcohol does not interfere with the determination of the nitrate group; nevertheless, the presence of considerable amounts of other alcohols leads to low results and the nitrometric method cannot be used. It is interesting to note that dialkylnitrosamines not only do not react themselves but they do not interfere with the determination of nitric acid either.

SUMMARY

1. In contradiction to published results, the capacity to be reduced in a Lunge nitrometer to nitric oxide is not a characteristic of N-nitroso and N-nitro groups. Aliphatic and alicyclic nitrosamines and nitramines do not react with mercury and concentrated sulfuric acid in the cold.

2. The nitrometer method cannot be universally employed for the analysis of alkyl nitrates. Methyl nitrate can be determined satisfactorily by this method but it is not applicable to ethyl nitrate.

3. Whether or not nitric acid can be determined in the presence of considerable amounts of organic compounds requires experimental verification in each individual case. Methyl alcohol and dialkyl nitrosamines do not interfere with the determination of nitric acids in the nitrometer.

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CRITICISM

N. I. Blok. Qualitative Chemical Analysis, Moscow-Leningrad.

State Chem. Press, 1952, p. 668, Print 10,000 Price 22 roubles 25 kopeks

A gap in Russian textbooks on qualitative chemical analysis is to some extent filled by N. I. Blok's book.

Both the negative and positive aspects of the textbook are discussed in this review.

In his introduction in the first part of the book (there are five parts in all) the author correctly points out that Russian scientists occupy a prominent position both in the history of analytical chemistry and in the history of chemical science in general; they have developed many of the most important fields of this science. Unfortunately, the author does not mention the huge developments made in analytical chemistry since the October Socialist Revolution, nor the names of the foremost Soviet analysts (N. A. Tananaev, I. V. Tananaev, I. P. Alimarin, A. M. Dymov, etc.).

The book starts with an exposition of the theoretical basis of analytical chemistry. The special chapter on "The D. I. Mendeleev periodic law and the analytical classification of ions" favorably distinguishes this book from other similar textbooks. This chapter includes results of the author's work which shows the significance of the periodic law for analytical chemistry. N. I. Blok is absolutely right in affirming that the classification of cations, which is related to the varying solubility of the metallic sulfides, is a logical outcome of the periodic law. Thus, the earlier artificial division of cations into analytical groups according to the solubilities of their salts actually depends on the position of the metal in the periodic system.

This very valuable chapter clarifies anew the division of cations into groups based on the classical hydrogen sulfide method. It must be emphasized that such an understanding of the analytical classification, which is absent in other textbooks on qualitative analysis, is of great significance in the methodological sense. By describing the individual analytical groups, the author starts from the right position, thanks to which all the material in the book is considered from one viewpoint, and this makes it valuable and complete.

In the succeeding chapters of the first part, the author sets forth the law of mass action, chemical equilibrium, solubility product, hydrogen ion concentration, hydrolysis, etc.

With regard to this part the following observations may be made. In expounding the theory of electrolytic dissociation and the role of I. A. Kablukov in the development of views on solution processes (vide p. 50), he should first of all have said something about D. I. Mendeleev's theory of hydration, and then followed this with its relation to the theory of electrolytic dissociation, and subsequently discussed I.A.Kablukov's vies, which are necessary for uniting the two theories. The author pays little attention to the accompanying reactions of coprecipitation, although they play an important part in reactions of separation.

In the author's words "the nature of ionic coprecipitation is variable" (p. 130) and the process is explained by him, as well as other phenomena, by successive precipitation. One cannot agree with this. The nature of coprecipitation can be ascribed to various causes: adsorption, formation of mixed crystals, chemical combination or occlusion, but it cannot be explained by successive precipitation since this phenomenon itself still remains to be explained.

A separate chapter is devoted to oxidation-reduction reactions. Considering the importance of oxidation-reduction processes in chemical analysis, one cannot be satisfied with the small number of examples - and those of the simplest - given here.

The author has made a number of errors in describing various oxidation reactions.

One cannot talk about oxidation in connection with the effect of hydrogen peroxide on vanadium and chromium salts when the valency of the elements is not changed. A similar error has been made in describing the formation of perchromic acids. The author states that "they are prepared by the oxidation of chromic acid with hydrogen peroxide" (p. 249). But chromium is quinquevalent in perchromic acid, while both in chromates and bichromates this element is hexavalent. He makes the same mistake when talking about the oxidizing action of hydrogen peroxide on ammonium molybdate in ammoniacal media (vide p. 469). From the formula adduced there, it is obvious that the valency of molybdenum does not change.

In the chapter on the application of organic reagents a formal list of the reagents is given. Before describing the reagents themselves however, he should have set out the theoretical principles of their action, e.g. the presence of atomic groups used for detecting particular elements.

The second part contains a description of special reactions for cations of various groups. The characteristics of each group is given before a description of the group, while in conclusion a systematic scheme of analysis is given. Analytical procedures are given for all five analytical groups. The author acquaints the reader with the electronic structures of each group and also with the ionic potential of the cations considered. The ionic potentials are compared with the base strength of the respective metals in separate tables. In this way N. I. Blok has attempted to come to a new characterization of the ions, and has given a deeper understanding of the properties of their compounds.

It is a pity that the reactions and the analytical procedure are only given for individual rare elements - this is insufficient.

A textbook which contains a large amount of material should include more data on the rare elements. Without their inclusion this part of the book leaves an impression of incompleteness. The sensitivity and specificity for each special reaction should have been given but have not. Little attention has been given to systematic analysis. In describing it and individual operations, only passing reference has been made to the amount of a cation that can thereby be determined. In such a case not only a qualitative but also an approximately quantitative evaluation of the cation present should have been given; this would lead to more accurate and careful work. All analytical operations should have been described in more detail, and any difficulties likely to be met in carrying out these reactions explained.

Special reactions and analytical procedures for anions make up the contents of the third part of the book. 19 acids are considered. Reactions for arsenic and arsenious acids are given in the section on cations.

In considering the classification of anions the author points out the absence of a "built up systematic analytical procedure for anions" (p. 487) and also the absence of reagents which enable the anion to be quantitatively separated into groups, which is necessary for detecting them in individual portions of test solution. One should add to this that a large number of schemes for the analysis of anions has been put forward and the expediency of using the different schemes considered many times; none of them have, however, achieved any practical significance hitherto. It should be possible to mention the reactions underlying such schemes and their drawbacks.

Nothing is said in this book about such acids as manganic, chromic, ferrocyanic, and acetic acids. Oxidation and reduction reactions which play such an important role in anion analysis are not considered. The presence of anions which possess both oxidizing and reducing properties in the mixtures being analyzed leads to complications for the analyst. This problem is not discussed in this book; neither is the respective analytical procedure described.

Procedures for anion analysis as a whole or for the determination of individual anions are not treated in sufficient detail. As an example we may quote the method of preparing sodium carbonate extracts, where a number of operational details which are essential for carrying out the extraction and for an understanding of the reactions which occur during this are omitted. The same applies to sulfate ion determination. Complications which might ensue are not pointed out.

Special methods, such as microcrystalloscopy and spot analysis, comprise the fourth section of the book. Their inclusion in a book on qualitative analysis is justified.

More should have been said about chromatographic analysis, and examples of its application in qualitative analysis given.

Systematic qualitative analysis is described in the last part of the book. The material is set out fairly completely and systematically. The author is correct in paying considerable attention to alloy analysis.

We should like to make some special observations. The choice of an acetate buffer to show how little the pH changes on addition of hydrochloric acid or sodium hydroxide (see p. 102) is unfortunate. This change cannot be regarded as insignificant when the pH values are 4, 5 and 6. The use of the term "silicomolybdic acid" is doubtful (vide p. 159). The expression "individual molecules stick together" is unfortunate (p. 125).

In places the material could be set out more clearly. The student cannot understand E_0 in Nernst's equation (p. 143) since normal potential is not discussed until pp. 145-146.

There are some misprints. The formulasgiven for tartaric acid, p. 148, and for manganese oxalate, p. 150, are wrong.

In a final summing of a book designed for students, and for workers in analytical laboratories and chemical factories, we can say that its undoubted merits, particularly the original treatment of the principle of analytical classification of cations, makes it worth while working further on this book to eliminate its drawbacks.

N. A. Rudnev

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CHRONICLE

CONFERENCE ON CHROMOTOGRAPHY

The V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry of the USSR Academy of Sciences, in conjunction with the commission on chromatography of the Division of Chemical Science of the USSR Academy of Sciences, intends to call a conference in November, 1953, on the application of M. S. Tsvet's chromatographic method in analytical chemistry.

The conference will hear reports on the application of adsorption, partition (including paper chromatography), ion-exchange, and precipitation chromatography, for the analysis of mixtures of organic and inorganic compounds. Testing of sorbents will also be discussed.

Those wishing to participate in the conference should communicate with the Organizing Committee at the following address:

Moscow, 49, P. O. Box 3085

From the Division of Chemical Science of the USSR Academy of Sciences

The Section of Chemical Sciences of the USSR Academy of Sciences wishes to announce to all chemists, and scientific and engineering-technical workers in other branches of science working on chemical problems in research institutes, higher educational institutions, and factory laboratories that it intends to hold a conference on chemical kinetics and reactivity in Moscow during 1953.

In addition discussions will also be held at the conference on such important theoretical questions as the relation between quantities such as velocity constants, activation energy, and steric hindrance; the part played by free radicals in ionic and chemical transformations; the nature of the activation of molecules in homogeneous and heterogeneous reactions; the basic types of chemical transformations (chain mechanism, ionic, simple molecular) and their occurrence; the nature of the effect of the media on the course of chemical reactions; methods of building up a theory of chemical processes on the basis of molecular structural theory, etc..

The Division of Chemical Sciences considers it essential that attention should be given to the role and significance of chemical kinetics in chemical technology.

As a result of the conference a concrete program should be mapped out for coordinating the work of physical and organic chemists on questions relating to the theory of chemical processes and the direction of research activity in chemical kinetics which can serve as a basis for further systematic developments in this branch of chemistry.

Reports will be read at the conference dealing with the theoretical problems of chemical kinetics, chemical kinetics in organic chemical reactions, and the chemistry and chemical kinetics of catalytic processes. Side by side with these reports, papers will be read on the results of original work, both practical and theoretical, of direct importance to the theme of the conference. Theses, and if possible the actual text of any reports to be read should be sent to the Organizing Committee of the Conference.

Address. Organizing Committee; Moscow.
B. Kaluzhskaya 31, Section of Chemical
Sciences USSR Academy of Sciences.

CHEMISTRY IN THE PUBLICATIONS OF THE ACADEMY OF SCIENCES

No. 2, 1931-1935. Compiled by O. P. Kamenogradskaya and V. P. Alekseev

(Chemical Literature of the USSR, Vol. No. 1, Issue 2. Edited by V. P. Barzakovsky and K. I. Shafranovsky, with a foreword by O. E. Evyagintsev), 1951, 245 pp., with illustrations. Price 15 roubles, 30 kopeks, bound.

1276 separate books on chemistry published by the USSR Academy of Sciences during 1931-1935 are included.

The book is on sale at all "Akademkniga" book shops.

Foreign orders should be sent to the Office of the Akademkniga, Moscow, B. Cherkassky, 2.

NIKOLAI DMITRIEVICH ZELINSKY

Academician Nikolai Dmitrievich Zelinsky, a foremost organic chemist and a Hero of Socialist Labor, died on July 31, 1953 in his 93rd year.

With Nikolai Dmitrievich Zelinsky's death we have lost a remarkable man and a scientist whose discoveries gained him world renown.

He was born on February 6, 1861. He received his higher education at Odessa University. In 1893, being already famous as a scientist, Nikolai Dmitrievich was invited to become a professor of organic and analytical chemistry in Moscow University. From this time his scientific and pedagogical activities were indissolubly bound up with Moscow University.

Zelinsky was a scientist with a profound and wide knowledge; his activities were numerous and varied.

His investigations in organic syntheses, catalysis, and in other fields of organic chemistry played a leading role in world science.

Starting at the time he entered Moscow University, he devoted his energies to developing the new and important branch of petroleum chemistry.

These investigations were of great practical importance, since they led to the production on an industrial scale of aromatic hydrocarbons from this raw material. Showing a profound interest in petroleum chemistry, Zelinsky devoted considerable labor to the development of methods of investigating the composition of petroleum and studying the nature of Russian petroleum and petroleum products. During the period when our country was sorely in need of aviation gasoline, he developed a new method for producing it from the fuel oil and petroleum available.

Zelinsky's work on proteins enabled an approach to be made to solving their structure.

Of exceptional importance is his work on the use of activated charcoal for adsorbing poison gases.

He also carried out a considerable amount of work in analytical chemistry. He improved the ninhydrin reaction for proteins, and gave a method for detecting cyclopentane hydrocarbons and a new quantitative method for the determination of fat in animal materials, etc.

Altogether he published 550 papers either on his own or in conjunction with his students.

In his scientific work he constantly attracted talented young research workers, as a result of which he created the most outstanding school of organic chemistry in the Soviet Union. His students work in research institutes, university, and factory laboratories. Many of them have been made active members of the Academy of Sciences of the USSR.

Zelinsky's name is very popular with us. We all knew his indefatigable struggle for peace and his fervent exhortation to scientists and to youth to defend peace.

The editorial board and the readers of the Journal of Analytical Chemistry together with all Soviet scientists are proud of the great scientist and fervent patriot of our country who devoted his life for the Socialist Fatherland.

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DISPERSOMETRIC METHODS FOR THE DETERMINATION OF AROMATIC HYDROCARBONS IN ADMIXTURE WITH HYDROCARBONS OF OTHER CLASSES

ANALYSIS OF MIXTURES NOT CONTAINING UNSATURATED COMPOUNDS

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New dispersometric methods for the determination of aromatic hydrocarbons in admixture with hydrocarbons of other classes have attracted the attention of many research workers during the last 10-15 years [1-8]. These methods are based on three assumptions: 1) the dispersion of a mixture is equal to the sum of the products of the dispersions of the individual components and their percentage content in the mixture (additivity rule); 2) the dispersion of all paraffin and naphthenic hydrdrocarbons is the same; 3) the dispersion of aromatic hydrocarbons differs considerably from the dispersion of paraffin and naphthene hydrocarbons.

Gross and Wackher [4] determined aromatic hydrocarbon content by specific dispersion calculated from the simplified equation:1)

$$\delta = \frac{n_F^t - n_C^t}{d_4^t} \cdot 10^4, \qquad (1)$$

where n_F and n_C are the refractive indices for the blue F and the red C line respectively of the hydrogen spectrum; d_4^t is the specific gravity; t is the temperature at which measurements are carried out. Mokhnatkin [2] in 1945, and a year later Ioffe [5] proposed the use of the relative dispersion1) for this purpose:

$$\omega = \frac{n_F^t - n_C^t}{n_D^t - 1} \cdot 10^3, \qquad (2)$$

where n_D is the refractive index for the yellow D line of sodium and the other legends have the same significance as in equation (1).

Quantitative determination of aromatic hydrocarbons by relative dispersion does not require determination of specific gravity, and it is therefore a more rapid method, and a smaller amount of test material is required. Nevertheless it was made clear later, that both the specific [6,7] and relative [7] dispersions deviate from the additivity rule; we also confirmed this. The deviation of the specific and relative dispersions from additivity for one of a series of mixtures which we examined is shown in the diagram. The amount of benzene in admixture with n-heptane is plotted on the abscissa, while the deviation of the experimentally determined values of the dispersion of the mixtures from the values calculated according to the additivity rule are plotted along the ordinate. In order to avoid errors caused by deviation from additivity during analysis, it has been suggested [6,7], that corrections be applied.

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1) In the papers cited [2,4,5] the equations do not contain the multiplier 10^n.

Mussaev [8], in 1949 showed that there is no need to introduce corrections if the benzene content of a mixture is determined by means of specific dispersion calculated from the difference in specific refractions (ΔR) for two lines (F, C) in the hydrogen spectrum[1]:

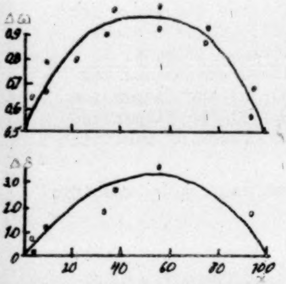
$$\delta_R = \Delta R\cdot 10^3 = \left[\frac{n_F^2 - 1}{n_F^2 + 2}\cdot\frac{1}{d_4^t} - \frac{n_C^2 - 1}{n_C^2 + 2}\cdot\frac{1}{d_4^t}\right]\cdot 10^3 = \left[\left(\frac{n_F^2 - 1}{n_F^2 + 2} - \frac{n_C^2 - 1}{n_C^2 + 2}\right) : d_4^t\right]\cdot 10^3, \quad (3)$$

where n_F, n_C, d_4^t, t have the same significance as in equation (1). This method however, just as the method based on equation (1), has the drawback that it requires determinations of the specific gravities of mixtures.

Having used various methods of determining aromatic hydrocarbon content in mixtures with hydrocarbons of other classes in the course of the present work, we concluded that it is possible to avoid the drawbacks mentioned above if we used the quantity ω_R for analysis; we call this quantity by analogy, the relative dispersion calculated according to the following equation:

$$\omega_R = \left[\left(\frac{n_F^2 - 1}{n_F^2 + 2} - \frac{n_C^2 - 1}{n_C^2 + 2}\right) : (n_D - 1)\right]\cdot 10^3, \quad (4)$$

where n_F, n_C, n_D have the same significance as in equations (1) and (2). Calculations based on equation (4) do not present any difficulty if refractometric tables [9] are used. Refractive indices were determined by means of a Pulfrich refractometer. When the Abbe refractometer was used the deviation in the values of the dispersion was too great, the method suggested by Ioffe [5] for the calibration of the refractometer is inaccurate. When the calibration curves suggested by Ioffe were used, considerable errors were sometimes obtained for the determination of aromatic hydrocarbon content.



Deviation of the specific (Δδ) and relative (Δω) dispersion from additivity for n-heptane-benzene mixtures. (x - benzene content % weight).

Since we wished to compare the accuracy of the various dispersometric methods for the determination of aromatic hydrocarbons, we have confined ourselves in the present article to a consideration of results obtained for the dispersion of paraffin, naphthene and aromatic hydrocarbons and their mixtures.

The relation between dispersion and composition was studied on synthetic binary mixtures of n-hexane-benzene, n-heptane-benzene, n-heptane-toluene, and methylcyclohexane-benzene. The results of measurements show that for mixtures of methylcyclohexane-toluene the relative dispersions are additive whether they are calculated according to equation (2) or equation (4). At the same time, dispersions calculated according to equations (1) and (2) for the first three mixtures and for mixtures of cyclohexane-benzene (from Pavlov's results [10]) do not follow the additivity rule. If the aromatic hydrocarbon content is then calculated according to the additivity rule, the error may amount to 2-4% weight. Nevertheless, the dispersions of these same mixtures when calculated according to equation (3) or according to the equation which we have proposed in this article, viz. equation (4), are additive, i.e., the relation between dispersion and aromatic hydrocarbon content in the mixture is graphically expressed by a straight line, and the deviations for determination of benzene or toluene content lie within the limits of experimental error (0.8-1.3%).

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[1] See footnote to page. 275.

TABLE 1

Average values of ω, δ, ω_R and δ_R for paraffin and naphthenic hydrocarbons of different molecular weight

Hydrocarbons	No. of hydrocarbons from which the mean was taken	ω	δ	ω_R	δ_R
Paraffins C_7	9	17.41	97.9	93.6	52.90
Paraffins C_8	8	17.30	97.3	91.7	51.56
Alkylcyclopentanes C_7.	6	17.65	96.7	93.6	51.35
Alkylcyclopentanes C_8.	8	17.54	96.4	92.7	52.08
Methylcyclohexane C_7 .	1	17.80	97.9	93.6	51.47
Alkylcyclohexanes C_8 .	4	17.72	94.3	92.6	50.96
Alkylcyclohexanes C_{10}.	4	17.55	95.3	90.4	49.77
Mean	39	17.50	96.5	92.6	51.44

Notes. ω, ω_R and δ_R were calculated by us, while the values for δ were taken from published results [12].

In order to calculate the degree of constancy of the relative and specific dispersions of the paraffin and naphthene hydrocarbons we used published results for 61 hydrocarbons [11-13]. From Table 1 it is obvious that the mean values of δ, ω, δ_R, and ω_R change only insignificantly with molecular weight and hydrocarbon structure. Nevertheless the differences between the dispersions of individual hydrocarbons can be considerably greater. Thus, ω_R for 2,2-dimethylpentane is equal to 96.57, while for secondary butylcyclohexane it is 89.09, i.e. the difference in dispersion amounts to 7.48. In the determination of the benzene content of a binary mixture with a paraffin or naphthene hydrocarbon, the maximum possible error which can arise as a result of deviations of the value of the dispersion of paraffin or naphthene hydrocarbons from its mean value increases in the order : ω, δ, ω_R and δ_R. This error is equivalent in percentage weights of benzene to: 3.5; 4.4; 5.4 and 8.7. In practice, if average values for the dispersion of the paraffin-naphthene part are used, this error will be less than the maximum value adduced above. If more accurate results are desirable, the actual value of the dispersion of the non-aromatic part of the mixture must be found. If the composition of the aromatic part of the mixture is known and results are available for the dispersion of the components making up the mixture, the dispersion of this part can be easily calculated by the additivity rule. In other instances (particularly for a series of analyses) the dispersion will have to be determined experimentally, the aromatic hydrocarbons in 1-2 ml of the mixture being removed by adsorption on silica gel or by sulfonation. Thus, during the determination of the toluene content of synthetic mixtures with dearomatized gasolines or ligroins, the relative dispersion of the non-aromatic was determined first; the error in the determination of the aromatics was therefore less than 1% weight.

TABLE 2

Dispersions of aromatic hydrocarbons

Hydrocarbons	ω	δ	ω_R	δ_R
Benzene	33.32	190.0	165.4	94.32
Toluene	32.28	185.0	160.8	92.62
Ethylbenzene	30.57	174.9	152.8	87.42
o-Xylene	31.41	180.4	155.7	89.41
m-Xylene	31.45	181.0	157.3	90.49
p-Xylene	31.68	182.4	157.9	90.49
Average for C_8	31.27	179.7	155.9	89.56
n-Propylbenzene	29.18	166.6	145.3	82.94
Isopropylbenzene	29.03	165.6	145.5	82.97
1-Methyl-2-ethylbenzene	30.08	172.4	149.2	85.50
1-Methyl-3-ethylbenzene	30.20	173.5	150.4	86.41
1-Methyl-4-ethylbenzene	30.24	173.8	151.1	86.85
1,2,3-Trimethylbenzene	30.58	175.8	150.4	86.43
1,2,4-Trimethylbenzene	30.90	178.1	153.1	88.15
1,3,5-Trimethylbenzene	30.75	177.5	158.2	88.07
Average for C_9	30.12	172.9	150.4	85.91
n-Butylbenzene	28.01	159.5	140.3	79.87
Isobutylbenzene	28.18	160.7	141.4	80.64
Sec.-butylbenzene	27.96	159.0	139.9	79.53
Tert.-butylbenzene	27.98	159.1	140.0	79.63
1,2-Diethylbenzene	29.02	166.2	144.8	82.84
1,3-Diethylbenzene	29.10	166.9	144.9	83.11
1,4-Diethylbenzene	29.30	168.2	146.1	83.87
Average for C_{10}	28.51	162.8	142.5	81.36

Notes. ω, ω_R and δ_R were calculated by us, while the values for δ were taken from published results [12].

Differences between the values of the dispersion of the aromatic hydrocarbons and the non-aromatic part of the mixture also affects the accuracy of the dispersometric analysis. Results adduced in Table 2 show that with increasing molecular weight of the aromatic hydrocarbons, the value of their dispersion decreases and thereby decreases the accuracy of determination. Thus, a measurement of the refractive index to an accuracy of 0.00005 can lead to an error of 0.7 for benzene, 0.9 for toluene, and 1.2% weight for aromatic hydrocarbons of C_{10} composition.

EXPERIMENTAL

Measurement of the Refractive Index of Light. A Pulfrich refractometer was used for the determination of refractive indices. The source of light was either a hydrogen spectrum tube or a gas burner colored by sodium chloride vapors. The refractometer was thermostated by means of an ultra-thermostat. The thermometers used for temperature measurement of the refractometer were checked against the melting point of ice prepared from twice-distilled water, and the conversion point of sodium sulfate decahydrate (Glauber salts) recrystallized four times [14]. The null point of the refractometer was checked against twice-distilled water, distilled before the determination from a quartz flask. The refractive index of water as determined on our apparatus was $n_D^{20} = 1.33300$, i.e. the same as the published value [15]. Numerous experiments which were carried out showed that the deviations in the determination of benzene and toluene contents in the same mixture but by different operators amounted to 1-1.5% weight.

TABLE 3

Constants of the hydrocarbons

Hydrocarbons	B.p. in °C at 760 mm	n_F^{20}	n_D^{20}	n_C^{20}	d_4^{20}	ω	δ	ω_R	δ_R
n-Hexane	68.5-68.8	1.37970	1.37515	1.37326	0.6590	17.17	97.8	93.3	53.12
n-Heptane. . . .	98.2-98.4	1.39237	1.38764	1.38570	0.6836	17.20	97.3	92.8	52.64
n-Octane	125.5	1.40238	1.39762	1.39552	0.7027	17.25	97.6	92.6	52.37
Cyclopentane . .	49.3	1.41140	1.40638	1.40429	0.7452	17.50	–	93.3	–
Cyclohexane. . .	80.6	1.43147	1.42615	1.42400	0.7783	17.52	96.0	92.0	50.37
Methylcyclohexane	100.7-100.9	1.42835	1.42297	1.42087	0.7691	17.64	96.7	93.2	51.23
Benzene.	80.1	1.51305	1.50100	1.49635	0.8789	33.29	189.8	165.5	94.33
Toluene.	110.6	1.50831	1.59681	1.49235	0.8672	32.12	184.1	160.0	91.79

Original Hydrocarbons. n-Hexane and n-heptane were prepared by purification of the commercial products. n-Octane was made by hydrogenation of caprylene over platinized carbon [16], the caprylene being made by dehydrogenation of secondary octyl alcohol over alumina. Cyclohexane and methylcyclohexane were prepared by the hydrogenation of benzene and toluene respectively in an autoclave in the presence of nickel. All the saturated hydrocarbons were treated with concentrated sulfuric acid, washed with soda and water and dried over calcium chloride. Cyclohexane and methylcyclohexane after purification of the latter from traces of toluene by passing through silica gel gave a negative formolite reaction. Benzene (cryoscopic) was treated with a small amount of concentrated sulfuric acid, washed, dried and frozen three times. Toluene (commercial) was sulfonated and the toluene sulfonic acid hydrolyzed. The toluene formed was washed and dried. All the hydrocarbons were distilled through a column with an efficiency equivalent to 50 theoretical plates.

The constants obtained for these pure hydrocarbons are given in Table 3. These constants in most cases agree with published results [11-13]. Any differences lie within the experimental errors.

Investigation of Synthetic Binary Mixtures. A study of the mixture n-hexane-benzene (Table 4) showed that the relative dispersions of these mixtures calculated from equation (2) do not follow the additivity rule. The relative dispersions of these mixtures calculated according to equation (4) are additive. The same applies to the dispersions of mixtures of n-heptane-benzene (Table 4) and n-heptane-toluene (Table 5). The specific dispersion of the mixtures n-heptane-toluene, calculated according to equation (1), do not follow the additivity rule. At the same time the specific dispersion calculated according to the differences in the specific refractions (equation 3) are additive. Determinations of the relative dispersion of mixtures of methylcyclohexane-toluene (Table 5) showed that the relative dispersion calculated according to equations (2) and (4) are additive.

TABLE 4

Dispersions of Mixtures

Weight % benzene	n_F^{20}	n_D^{20}	n_C^{20}	d_4^{20}	ω	δ	ω_R	δ_R
				n-Hexane-benzene				
0	1.37970	1.37575	1.37326	-	17.17	-	93.3	-
10.86	1.38991	1.38480	1.38272	-	18.68	-	101.1	-
36.48	1.41733	1.41071	1.40805	-	22.59	-	119.8	-
47.82	1.43125	1.42388	1.42091	-	24.39	-	128.1	-
55.98	1.44195	1.43396	1.43079	-	25.71	-	134.3	-
64.97	1.45496	1.44696	1.44283	-	27.17	-	140.3	-
70.41	1.46250	1.45334	1.44975	-	28.12	-	144.7	-
82.23	1.48133	1.47116	1.46717	-	30.28	-	152.6	-
100	1.51305	1.50100	1.49635	-	33.29	-	165.5	-
				n-Heptane-benzene				
0	1.39237	1.38764	1.38570	0.6836	17.20	97.3	92.8	52.64
3.81	1.39534	1.39038	1.38844	0.6841	17.67	100.8	95.3	54.37
10.39	1.39901	1.39372	1.39162	0.6988	18.58	105.7	101.1	56.95
34.11	1.42331	1.41671	1.41403	0.7358	22.27	126.1	117.6	66.59
75.98	1.47545	1.46481	1.46104	-	29.04	-	148.2	-
93.51	1.49963	1.48833	1.48395	0.8612	32.11	182.1	161.0	91.26
100	1.51305	1.50100	1.49635	0.8789	33.29	189.8	165.5	94.33

TABLE 5

Dispersions of Mixtures

Weight % toluene	n_F^{20}	n_D^{20}	n_C^{20}	ω_R	ω_R
		n-Heptane-toluene			
0	1.39237	1.38764	1.38570	17.20	92.6
9.25	1.40128	1.39599	1.39394	18.53	99.5
23.41	1.41351	1.40754	1.40520	20.39	108.7
38.17	1.42840	1.42156	1.41886	22.63	119.3
40.21	1.43116	1.42417	1.42141	22.98	120.6
61.45	1.45544	1.44707	1.44378	26.07	134.9
73.40	1.46983	1.46058	1.45696	27.94	143.3
89.25	1.49092	1.48043	1.47633	30.37	153.2
100	1.50831	1.49681	1.49235	32.12	160.0
		Methylcyclohexane-toluene			
0	1.42835	1.42297	1.42087	17.64	93.2
17.72	1.43982	1.43356	1.43104	20.24	105.8
37.83	1.45596	1.44661	1.44565	23.08	119.1
44.47	1.45918	1.45139	1.44830	24.10	124.3
53.08	1.46614	1.45783	1.45453	25.36	130.0
94.50	1.50262	1.49155	1.48724	31.28	156.4
100	1.50831	1.49681	1.49235	32.12	160.0

TABLE 6

Determination of Toluene in Synthetic Mixtures

% Weight of toluene in the original mixture	% Weight of toluene found by the relative dispersion	Difference between amount taken and found in %
	With Dearomaticized gasoline	
52.61	52.98 51.86	+ 0.37 − 0.75
62.10	62.10 60.87	0.00 − 0.23
83.27	83.36 82.75	+ 0.11 − 0.52
	With Dearomaticized Ligroin	
24.59	24.58	− 0.01
48.19	48.07	− 0.12
50.80	50.20	− 0.60

Investigation of Synthetic Mixtures of Toluene with Dearomaticized Gasoline and Ligroin. In order to check on the applicability of the method based on relative dispersion calculated according to the equation which we have proposed, viz equation (4), to the determination of the aromatic hydrocarbon content of petroleum fractions, we analyzed synthetic mixtures of toluene with dearomaticized gasoline and ligroin. The results given in Table 6 show that the method is applicable.

In conclusion we should like to thank E. A. Mikhailova for a gift of a mixture of n-heptane-benzene, T. F. Bulanova for some cyclopentane and Z. N. Parnes for a sample of twice distilled water.

SUMMARY

1. A comparison has been made of four dispersometric methods for the determination of the aromatic hydrocarbon content of mixtures with paraffin and naphthene hydrocarbons. It has been shown that a method which is put forward in the present article has the advantage that there is no need to determine specific gravity neither does it require the introduction of corrections in the analysis of mixtures containing benzene and toluene.

2. The dispersion of mixtures of different composition has been determined: n-hexane-benzene, n-heptane-benzene, n-heptane-toluene, and methylcyclohexane-toluene.

3. It has been found that for the binary systems examined the relative dispersion (ω_R) calculated according to theequation

$$\omega_R = \left[\left(\frac{n_F^2 - 1}{n_F^2 + 2} - \frac{n_C^2 - 1}{n_C^2 + 2}\right) : (n_D - 1)\right] \cdot 10^3,$$

follows the additivity rule and can therefore be used for the determination of aromatic hydrocarbons in admixture with paraffin and naphthene hydrocarbons.

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A STUDY OF THE REACTION RATES OF PROCESSES OCCURRING DURING POTENTIOMETRIC TITRATION

L. Ya. Polyak and B. N. Kabanov

Many chemical reactions cannot be used in potentiometric analysis because of the slow rate at which they occur and also because of the slow rate at which the electrode potential is established even when other factors are favorable.

A study of the reasons for these phenomena and also of the establishment of conditions which speed up these processes is of both practical and theoretical interest. Hitherto only a few attempts have been made to investigate and explain the processes which occur during potentiometric titration, by electrochemical means. A large amount of the material published relating to potentiometric analysis is a description of individual and empirically worked out methods.

The system $Fe(CN)_6^{3-}$ – $Fe(CN)_6^{4-}$ is of particular interest in potentiometry, since a number of metals form difficultly soluble ferrocyanides. Many authors [1,2,3] point out that the wide application of ferrocyanides in potentiometric analysis is faced by a number of difficulties, the most important of which is the slowness with which potentials are established during titration. It is for this reason that the precipitation of zinc with ferrocyanide, which was suggested as long ago as 1909 and which was afterwards studied by a number of research workers, has up to recently [4], not been widely used in practice. Attempts have been made to surmount the difficulty pointed out above by replacing direct titration of zinc with ferrocyanide by a back titration of excess ferrocyanide with permanganate [2], or the precipitation of zinc by ferrocyanide is used in other physico-chemical methods of analysis; drop-tempometric [3] and amperometric titrations.

We considered it expedient to use electrochemical methods – i.e., taking polarization curves and determining potential changes with time – for the study, under various conditions, of the kinetics of the rate at which the potential is established in the oxidation-reduction system $Fe(CN)_6^{3-}$ – $Fe(CN)_6^{4-}$ which determines the potential during the titration of a number of metals: zinc, cadmium, lead, copper, etc., with ferrocyanide.

In the work described, the effect of the following factors on the rate at which the electrochemical reactions proceed on a platinum electrode in the system $Fe(CN)_6^{3-}$ – $Fe(CN)_6^{4-}$ was studied:

a) the effect of the concentration of the ions which determine the potential;
b) the effect of other electrolytes.

It was of interest to determine the rate of the electrode processes near the equilibrium potential at a point where the solution had the composition we were interested in, since in the case of low reaction rates during potentiometric titration, deviation from the equilibrium potential and distortion of the potentiometric curves are possible.

In addition to making electrochemical measurements during direct potentiometric titrations, the effect of the factors mentioned above on the rates at which the chemical processes in solution proceed was also studied.

A. N. Frumkin has given a kinetic equation for electrochemical processes [5]. At the basis of this equation is the assumption that the rate of both forward and reverse processes is a function of the structure of the double electric layer on the metal-solution boundary, of the potential jumps, concentration, etc. During the flow of a current through an electrode the overall rate of the process is equal to the difference in velocities of the forward and reverse processes. A. N. Frumkin's equation, which was primarily deduced for the evolution of hydrogen, remains valid for the case of an oxidation-reduction system under such conditions where the reactions of accepting or donating ions, e.g.

$$Fe(CN)_6^{3-} + e \longrightarrow Fe(CN)_6^{4-},$$

also proceed with a terminal velocity.

Mention must be made of some work which should be considered in connection with the problem under discussion. A. L. Rotinyan's work [7,8] is devoted to the kinetics of the establishment of the potential in the systems $Tl^{3+} - Tl$ and $AsO_3^{3-} - AsO_4^{3-}$.

Esin, Derendyaev, and Ladygin [9], found that the systems $Fe(CN)_6^{3-} - Fe(CN)_6^{4-}$ and $Fe^{3+} - Fe^{2+}$ do not display chemical polarization on pure platinum electrodes; this means that the rate at which the potential of the platinum electrode is established in these systems is restricted only by diffusion. In potentiometric practice however, it is not possible to achieve that degree of freedom of the solution and electrode from contamination by surface active materials which guarantees the absence of overvoltage in the work cited. Garmody and Rohan [10], investigated the polarization of platinum and gold electrodes in neutral and alkaline ferrocyanide solutions, and showed that on taking into account concentration polarization, chemical polarization can also be observed in the system. They, however, worked with very high concentrations which are of little interest for potentiometry. Coursier [15], found that platinum ceases to act as an electrode for the system $K_3Fe(CN)_6 - K_4Fe(CN)_6$ (pH 5.9, ionic strength 1), when the concentration of $K_3Fe(CN)_6$ is less than 10^{-5} g-ion liter (in an atmosphere of hydrogen) or less than 10^{-4} g-ion/liter (in an inert gas atmosphere).

We reckon that it is essential to compare the results of potentiometric measurements and polarization curves in order to explain the reason for the slowness with which potentials are established during titration; whether it is the result of the slowness of the electro-chemical reaction itself, viz a change from one form of oxidation of the ion to another, which takes place on the electrode, or the slowness of the chemical processes occurring in solution – the interaction of metals ions with ferrocyanide ions.

Method of Measurement

Measurement of overvoltage and the rate at which equilibrium potentials are established on a platinum electrode were made by the usual compensation method, using a saturated calomel electrode as reference electrode. The polarization set up is shown in Fig. 1. The potentials of the polarized platinum electrodes are calculated with respect to the normal hydrogen electrode. Measurements were made at room temperature within a current density range for the polarization current of 10^{-5} to 10^{-2} A/cm^2. In order to decrease the concentration polarization of the solution during measurements the solution was stirred by bubbling nitrogen through it. Both electrodes, test and reference, were immersed in one solution in order to avoid changes in the composition of the solution with time. Before taking each curve the electrode was washed with water and heated in the oxidizing flame of a gas burner.

When the electrode had been immersed in the oxidation-reduction system, the equilibrium potential of the electrode was measured, the electrode was then subjected to polarization by a steadily increasing current. Usually we first took the curves for cathodic polarization, and then the anodic polarization curves.

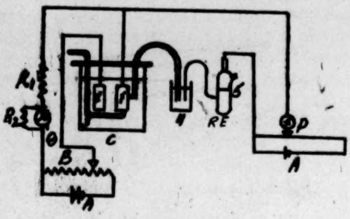

Fig. 1. Polarization setup. A)Accumulator, B) rheostat, G) galvanometer of sensitivity 1° = $0.39 \cdot 10^{-6}$ A, R_1 and R_2) resistance boxes of 10,000 Ω, P) potentiometer, C) polarization cell. 1) Polarized electrode, 2) supplementary electrode, 3) lead-in for nitrogen to stir up the solution, 4) communicating vessel, 5) saturated calomel half-element. RE) Reference electrode.

The potassium ferriferrocyanide solutions were prepared from analytical quality reagents. The solutions were shielded from light to avoid decomposition.

1. The Effect of the Concentration of the Potential-Determining Ions on the Polarization Curves.

In order to get a general characterization of the phenomena observed, we first of all took a series of curves for solutions containing potassium ferricyanide in concentrations from $1 \cdot 10^{-2}$ to $1 \cdot 10^{-5}$ mol per liter for the same ferrocyanide concentration of $1 \cdot 10^{-4}$ mol per liter (Fig. 2).

The next series of polarization curves (Fig. 3) was only taken for two concentrations of ferricyanide $2 \cdot 10^{-5}$ mol/liter and $2 \cdot 10^{-4}$ mol/liter for one concentration of ferrocyanide of $2 \cdot 10^{-5}$ mol/liter, these concentrations being those used in the potentiometric method of titrating zinc [1,4]. All the curves in Fig. 2 and two curves in Fig. 3 were taken in 1 M sulfuric acid, in accordance with the conditions of the potentiometric titration of zinc applied by one of the authors [4]; Curve 3, Fig. 3 was taken in 0.05 M sulfuric acid[1]. The large excess of $Fe(CN)_6^{3-}$ in comparison with the concentration of $Fe(CN)_6^{4-}$ in the case of Curve 1, Fig. 2 enabled us to measure the overvoltage of the reduction process of $Fe(CN)_6^{3-}$ reliably, since this excess increases the interval in the current density between the exchange current and the limiting current.

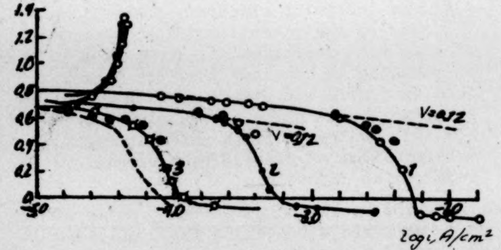

Fig. 2. Effect of the concentration of the potential determining ions on the shape of the polarization curves in the system $Fe(CN)_6^{3-}$ – $Fe(CN)_6^{4-}$:
1) $1 \cdot 10^{-2}$M $K_3Fe(CN)_6$; $1 \cdot 10^{-4}$M $K_4Fe(CN)_6$; 1M H_2SO_4;
2) $1 \cdot 10^{-3}$ $K_3Fe(CN)_6$; $1 \cdot 10^{-4}$M $K_4Fe(CN)_6$; 1M H_2SO_4;
3) $1 \cdot 10^{-4}$M $K_3Fe(CN)_6$; $1 \cdot 10^{-4}$ M $K_4Fe(CN)_6$; 1M H_2SO_4.
Crosses and circles denote electrode potentials corrected for concentration polarization.

2. The Effect of Other Electrolytes.

a) The Effect of Sulfuric Acid, and Potassium Sulfate.

Changes introduced by one of us into the existing potentiometric titration of zinc [4], consist among others in increasing the concentration of sulfuric acid from 0.05 to 1 M.

By increasing the acidity we tried in the first place to remove the influence of other elements present in the test alloys, e.g., magnesium, cerium,

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[1] In accordance with the conditions recommended by I. Kolthoff [1].

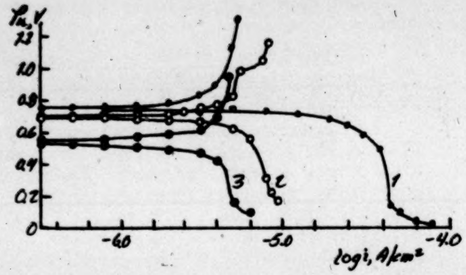

Fig. 3. Effect of sulfuric acid concentration on the shape of the polarization curves in the system $Fe(CN)_6^{3-} - Fe(CN)_6^{4-}$: 1) $2 \cdot 10^{-4}$M $K_3Fe(CN)_6$; $2 \cdot 10^{-5}$M $K_4Fe(CN)_6$; 1M H_2SO_4; 2) $2 \cdot 10^{-5}$M $K_3Fe(CN)_6$; $2 \cdot 10^{-5}$M $K_4Fe(CN)_6$; 1M H_2SO_4; 3) $2 \cdot 10^{-5}$M $K_3Fe(CN)_6$; $2 \cdot 10^{-5}$M $K_4Fe(CN)_6$; 0.05 M H_2SO_4.

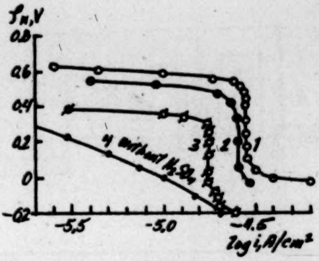

Fig. 4. The effect of sulfuric acid concentration on the shape of the polarization curves for the system $Fe(CN)_6^{3-} - Fe(CN)_6^{4-}$. For all curves $K_3Fe(CN)_6$–$1 \cdot 10^{-4}$M: $K_4Fe(CN)_6$ –$1 \cdot 10^{-4}$M: 1) 0.5 M H_2SO_4; 2) 0.05M H_2SO_4; 3) 10^{-4}M H_2SO_4; 4) without H_2SO_4.

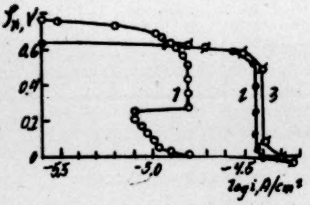

Fig. 5. The effect of Al^{3+} ions on the shape of the polarization curves for the system $Fe(CN)_6^{3-} - Fe(CN)_6^{4-}$: 1 $1.3 \cdot 10^{-4}$M $K_3Fe(CN)_6$; $1.3 \cdot 10^{-4}$M $K_4Fe(CN)_6$; 0.5 M H_2SO_4; 0.5 M Al^{3+}; 2) $1.3 \cdot 10^{-4}$M $K_3Fe(CN)_6$; $1.3 \cdot 10^{-4}$M $K_4Fe(CN)_6$; 0.54M H_2SO_4; 0.18 M Al^{3+}; 3) ditto, as 2 but without Al^{3+}.

zirconium, manganese) and the influence of difficultly soluble precipitates formed with potassium ferrocyanide in weakly acid solutions. The effect of sulfuric acid concentration on the shape of the concentration curves is shown in Curves 2 and 3, Figs. 3 and 4.

b) The Effect of Aluminum Salts. The effect of aluminum salts on the rate of the electrode reaction was considered separately. According to published data large quantities of aluminum make the platinum indicator electrode insensitive [1], during the potentiometric titration of zinc with ferrocyanide, from which it is possible to conclude that the aluminum ions interfere with the oxidation-reduction reaction taking place on the electrode. For this reason a direct potentiometric determination of zinc in aluminum alloys is regarded as impossible.

In connection with the practical solution by one of us of the problem of determining zinc in aluminum alloys [11], we aimed at checking this published material. In order to explain the behavior of a platinum electrode immersed in the system $Fe(CN)_6^{3-} - Fe(CN)_6^{4-}$ in the presence of aluminum salts we took polarization curves in 0.18 and 0.54 M solutions of Al^{3+}, these are adduced in Fig. 5.

3. Potentiometric Titration

Results for a series of experiments on the potentiometric titration of zinc under various conditions of mixing temperature and solution composition, which were carried out in order to check on published results and to explain the reason for the slow establishment of the indicator electrode potential, are given in Fig. 6. Curve 1 was taken in 1 M sulfuric acid in the presence of 0.2 M K^+ ions, since this corresponds to the conditions chosen by us for the titration of zinc [4]; Curve 2 was taken at the same concentration but in the absence of K^+ ions. Curve 3 was taken in the absence of sulfuric acid but in the presence of 0.2 M K^+ ions. Curve 4 was taken in the absence of both sulfuric acid and K^+ ions.

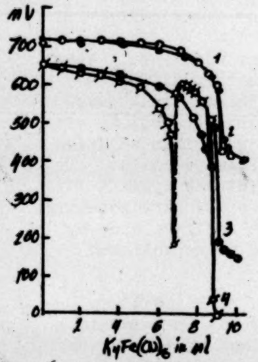

Fig. 6. Potentiometric curves for the titration of zinc with potassium ferrocyanide under various conditions. 1) In presence of H^+ and K^+ ions; 2) in presence of H^+ ions but in absence of K^+ ions; 3) in presence of K^+ ions but in absence of H^+ ions; 4) in absence of both H^+ and K^+ ions.

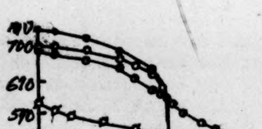

Fig. 7. Effect of aluminum ions on the potentiometric titration curves of zinc with potassium ferrocyanide solution: 1) In the absence of Al^+ ions; 2) in a solution where the concentration of Al^{3+}=0.36M; 3) in a solution where the concentration of Al^{3+}=0.54M; 4) ditto as 2 but the Al^{3+} ions are fixed as complexes with oxalic acid.

The results of the experiments aimed at clarifying the effect of aluminum salts on the curves for the potentiometric titration of zinc with ferrocyanide are given in Fig. 7. Curve 1 was taken in the absence of aluminum, Curves 2 and 3 were taken in solutions with aluminum ions concentrations of 0.36 and 0.54 M, Curve 4 was taken under the same conditions as Curve 2, but the aluminum ions were fixed as complexes with oxalic acid.

Discussion of Results

During the potentiometric titrations of zinc, cadmium, lead, and other metals with ferrocyanide, the metal ions do not participate in the process of establishing the potential of the platinum electrode. In order to facilitate the establishment of the potential during titration of these ions by ferrocyanide, some potassium ferricyanide was introduced into the solution. Thus, although precipitation reactions of the metallic ions with ferrocyanide occur in solution, we have in all such cases a typical oxidation-reduction system, the equilibrium potentials of which are determined by the equation:

$$\epsilon = \epsilon_0 + \frac{RT}{F} \ln \frac{a_{Fe(CN)_6^{3-}}}{a_{Fe(CN)_6^{4-}}} .$$

The experiments which we carried out on the potentiometric titration of zinc under various conditions showed that in neutral solutions which do not contain K^+ ions (Curve 4, Fig. 6), and also during the titration of zinc in the presence of aluminum salts (Curves 2 and 3, Fig. 7) the titration process is slow and the shape of the potentiometric curve is distorted. The question arises as to whether or not this is related to the slowness with which the electrode potential is established as indicated in the literature. In order to solve this question we must turn to an analysis of the polarization curves.

Cathodic polarization is accompanied by the reduction of $Fe(CN)_6^{3-}$ to $Fe(CN)_6^{4-}$ ions. The segment of Curve 1, Fig. 2 in the current density range between 10^{-4} and 10^{-3} A/cm^2 characterizes almost in a pure form the chemical polarization which is related to the slowness of the electron transfer process according to the reaction

$$Fe(CN)_6^{3-} + e \longrightarrow Fe(CN)_6^{4-}.$$

The coefficients of inclination (tangent) of the curve in various experiments is equal to 0.12-0.15 V. Thus, under these conditions the reaction occurs with an appreciable overvoltage. For a current density of roughly $5 \cdot 10^{-3}$ A/cm^2 for a given concentration and rate of mixing a limiting diffusion current is attained for the reaction. The slowing down of potential changes for current densities greater than $6 \cdot 10^{-3}$ A/cm^2 is determined by the process of hydrogen evolution on the electrode. When the $Fe(CN)_6^{3-}$ concentration is decreased 10 times the limiting diffusion current decreases approximately 10 times. On switching to an even lower concentration this proportionality is destroyed since a side reaction, viz., the ionization of oxygen, starts and this ionized oxygen goes into solution from the nitrogen passing through the solution (the nitrogen contains oxygen). Consequently, at low concentrations of the oxidizing agent $K_3Fe(CN)_6$ on the platinum electrode during titration, a stationary potential which is displaced from the equilibrium potential on the positive side by the action of an other oxidizing agent - oxygen - should be established instead of the equilibrium potential.

Anodic polarization is accompanied by the oxidation of $Fe(CN)_6^{4-}$ to $Fe(CN)_6^{3-}$ ions. Since the concentration of $Fe(CN)_6^{4-}$ ions was the same in all experiments, the curves of anodic polarization obtained agree very well among themselves.

We introduce a correction for concentration polarization to the curve for cathodic overvoltage on the basis of the limiting current density observed, $\underline{i}_d$, and the tangent b = 0.12-0.15 V. The magnitude of the correction for concentration polarization when overvoltage occurs [12], can be calculated by means of the formula

$$\Delta\varphi = - b \log \left(1 - \frac{i}{i_d}\right)$$

where $\underline{i}$ is the current density.

It is evident from Fig. 2 (where the corrected values are denoted by crosses within circles) that on approaching the limiting current the shape of the overvoltage curve clearly deviates from a straight line. It may be postulated that at high current densities a slow-down of the reaction occurs which is connected with the approach to the potential of a null charge of the platinum [6], the magnitude of which is somewhat greater than 0.2 V for a weakly oxidized platinum surface.

From these experiments it follows that in accordance with theory, in the region of potentials at which the concentration polarization is insignificant, the velocity of the cathodic process for ferrocyanide reduction increases proportionally to the concentration of $Fe(CN)_6^{3-}$ ions (Curves 1, 2, and 3, Fig. 2). Thus, with increasing concentration of oxidizing agent for equal differences between electrode potential and the potential of the solution, the reduction of the oxidizing agent speeds up. Consequently, the rate at which the equilibrium potential is established in the more dilute solutions will be less, since for equal capacities of the double layer, the change in its potential for the lower velocities of the electrochemical process will be slower.

We have derived a formula for the theoretical calculation of the time required to establish the equilibrium potential. It is known that for low values of the overvoltage, η may be approximately regarded as being a linear function of current density:

$$\eta = b'i. \tag{1}$$

On the other hand, the relation between the amount of electricity passed through the electrode in a time dt, and the potential change of the electrode $d\eta$ is related to the electrical capacity of the electrode C by the following equation:

$$idt = Cd\eta. \tag{2}$$

From equations (1) and (2) it follows that

$$dt = -b'C\frac{d\eta}{\eta}.$$

On integration we got

$$\int_0^t dt = -b'C\int_{\eta_0}^{\eta_t}\frac{d\eta}{\eta}; \quad t = Cb'\cdot 2.3\log\frac{\eta_0}{\eta_t} \tag{3}$$

where η_0 is the overvoltage at the beginning ($t = 0$), η_t is the overvoltage at time t. The value of b' can be found from equation (1) by means of Fig. 8, by taking into account that for a cathodic process, by definition $\eta = \varphi_0 - \varphi$, where φ_0 is the equilibrium electrode potential and φ the non-equilibrium potential. From Fig. 8, on which the first sections of the cathodic curves of Fig. 3 plotted in linear coordinates, are depicted, it is evident that in a solution of $2\cdot10^{-4}$M $K_3Fe(CN)_6$ (Curve 1) b' = 2000 Ω while in a solution of $2\cdot10^{-5}$M (Curve 2) b' = 10000 Ω; consequently the rate at which the potential is established is slower in the more dilute ferricyanide solution. For a change in potential of 0.1 V, i.e. for $\eta_{t=0} = 0.1$ V and for an accuracy of measurement of 0.001 V, i.e. at $\eta_t = 0.001$ V, we can get the times for the equilibrium potential to be established from formula (3):

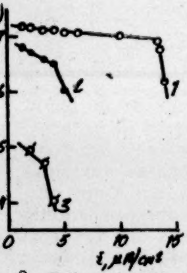

Fig. 8. Determination of coefficient b' in the system $Fe(CN)_6^{3-} - Fe(CN)_6^{4-}$: 1) $2\cdot10^{-4}$M $K_3Fe(CN)_6$; $2\cdot10^{-5}$M $K_4Fe(CN)_6$; 1M H_2SO_4; 2) $2\cdot10^{-5}$ M $K_3Fe(CN)_6$; $2\cdot10^{-5}$M $K_4Fe(CN)_6$; 1M H_2SO_4; 3) $2\cdot10^{-5}$M $K_3Fe(CN)_6$; $2\cdot10^{-5}$M $K_4Fe(CN)_6$; 0.05 M H_2SO_4.

for curve 1

$$t = 200\cdot10^{-6}\cdot2\cdot10^{3}\cdot2.3\log\frac{10^{-1}}{10^{-3}} = 1.8 \text{ sec.},$$

for curve 2

$$t = 200\cdot10^{-6}\cdot10\cdot10^{3}\cdot2.3\log 10^{2} = 9 \text{ sec.}$$

From this calculation it is obvious that for the solution compositions indicated the potential should be established in the course of seconds, i.e., it is obviously slow because of the overvoltage of the oxidation-reduction process.

However, a comparison of the rate at which the potential is established during potentiometric titration shows that the rate at which the electrode potential is established should not in practice limit the rate of potentiometric titration processes which occupy 30-50 minutes, according to the results of many authors [1,2].

In order to confirm the results of this calculation, the rate at which the equilibrium potential is established was verified experimentally. By means of cathodic and anodic polarization the electrode potential was adjusted to a definite value in the respective solutions, after which the polarization current was interrupted and the time rate at which the equilibrium value of potential was established was measured. These experiments showed that the experimental curves for the change of potential with time agree satisfactorily with theory; the electrode potential is established in the course of seconds and tens of seconds (Fig. 9; see page 294), with an accuracy of 1 mV.

Electrochemical experiments showed in this way that the slowness of the titration of zinc with ferrocyanide, to which many authors have referred, is not determined by the slow rate of the electrochemical oxidation-reduction process on the electrode. It may be postulated that this phenomenon is related to the slowness of the chemical processes in solution, and this is confirmed by experiments on the direct potentiometric titration of zinc under varying conditions (Fig. 6). None of the following factors seemsto have a decisive effect on the velocity of the titration process: temperature, mixing rate, method of addition and concentration of ferricyanide. The duration of titration increases sharply on switching over from titration in acid to titration in neutral solution, and if potassium sulfate is not added to the solution: instead of 6-8 minutes (Curves 1, 2 and 3, Fig. 6) the titration of an equal amount of zinc takes 45 minutes (Curve 4, Fig. 6). Apparently, under these conditions a compound is initially precipitated which is richer in zinc1), and which only reacts slowly with potassium ions to form a double salt of potassium-zinc ferrocyanide. Thus, the following reaction probably occurs in neutral solution:

$$2Zn^{2+} + Fe(CN)_6^{4-} = Zn_2Fe(CN)_6,$$

this is succeeded slowly (for structural reasons) by the reaction

$$2Zn_2Fe(CN)_6 + 2K^+ = Zn_3[KFe(CN)_6]_2 + Zn^{2+}.$$

When this occurs one quarter of the zinc which reacted initially is freed and an additional two thirds of a g-ion of ferrocyanide is expended in the formation of a mole of the double salt if 2 g-ions are required for the completion of the rapid reaction. That the reaction mechanism during titration in neutral solution is of this type is confirmed by the shape of the potentiometric curve (Curve 4, Fig. 6). The potential decreases rapidly when 3/4 of the amount of ferrocyanide needed for completion of the precipitation has been added. Only after 10-12 minutes does the potential rise again, to drop after the addition of new portions of ferrocyanide in an amount equal to 3/4 of that remaining, for completing the reaction.

We showed experimentally that the formation of a double salt of zinc and potassium ferrocyanide is speeded up in the presence of sulfuric acid. This may be explained by the fact that the $HFe(CN)_6^{3-}$ ion participates in the intermediate stage of the reaction; e.g. in a weakly acid solution (Curve 2, Fig. 6) the following reactions may probably take place rapidly

$$Zn^{2+} + HFe(CN)_6^{3-} = ZnHFe(CN)_6^- \; ; \quad 2ZnHFe(CN)_6^- + Zn^{2+} = Zn_3[HFe(CN)_6]_2,$$

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1) The possibility of such a reaction is confirmed by published results.

and these molecules exchange hydrogen for potassium relatively quickly. This exchange should be speeded up even more on increasing the potassium ion concentration in solution, as was confirmed by our experiments.

In even stronger acid solutions the following reactions probably occur

$$Zn^{2+} + H_2Fe(CN)_6^{2-} = ZnH_2Fe(CN)_6,$$

or

$$Zn^{2+} + H_2Fe(CN)_6^{2-} = ZnHFe(CN)_6^{-} + H^{+}.$$

and the reaction product can react without hindrance with zinc to form $Zn_3[HFe(CN)_6]_2$.

The basis for these assumptions is the fact that ferrocyanic acid does not dissociate completely. The constants for the third and fourth stages of dissociation of this acid according to Nekrasov and Zotov [14], are respectively equal to $K_3 = 10^{-3}$ and $K_4 = 5\cdot10^{-5}$. In 1 M acid solution, in which $[H^+] = 1$,

$$\frac{[HFe(CN)_6^{3-}]}{[H_2Fe(CN)_6^{2-}]} = \frac{10^{-3}}{[H^+]} = \frac{0.1}{100} .$$

In 10^{-3}M acid solution $[H^+] = 2\cdot10^{-3}$

$$\frac{[HFe(CN)_6^{3-}]}{[H_2Fe(CN)_6^{2-}]} = \frac{10^{-3}}{2\cdot10^{-3}} = \frac{33}{66}$$

(in 1 M solution, sulfuric acid practically dissociates only to the first stage and in 10^{-3}M solution to both stages). Further, in 10^{-3}M acid solution

$$\frac{[Fe(CN)_6^{4-}]}{[HFe(CN)_6^{3-}]} = \frac{5\cdot10^{-5}}{[H^+]} = \frac{5\cdot10^{-5}}{2\cdot10^{-3}} = \frac{0.82}{33} .$$

Consequently, in 1 M sulfuric acid solution the $H_2Fe(CN)_6^{2-}$ ion dissociates to H^+ and $HFe(CN)_6^{3}$ to the extent of 0.1%, and in 10^{-3}M sulfuric acid the extent of dissociation is 33%, while the $Fe(CN)_6^{4-}$ ions in the first case form to the extent of only 0.00001% and in the second case 0.8%.

A consideration of Curve 3, Fig. 3, which characterizes the effect of sulfuric acid concentration on the rate of the electrode reaction brings to light the fact that the equilibrium potentials of the ferri-ferrocyanide electrode in 1 M and 0.05 M solutions of sulfuric acid are strongly displaced relative to one another.

Ignoring the activity coefficients we can calculate approximately how much the equilibrium potential of the electrode will be displaced on switching from a 1 M to a 0.05 M solution of sulfuric acid.

If it is assumed that the electrode potential is determined by the equation

$$H_2Fe(CN)_6^{2-} = Fe(CN)_6^{3-} + 2H^+ + e,$$

then

$$\varphi = \varphi_0 + \frac{RT}{F} \ln \frac{[Fe(CN)_6^{3-}]\,[H^+]^2}{[H_2Fe(CN)_6^{2-}]}$$

Actually it follows from Fig. 3 that at high acid concentrations the equilibrium potential changes approximately proportional to the logarithm of the square of the hydrogen ion concentration. This fact confirms the correctness of the assumption that it is the $H_2Fe(CN)_6^{2-}$ ions and not the $Fe(CN)_6^{4-}$ ions which participate in the electrochemical reaction on the electrode at low pH's (0-2).

This assumption is also confirmed by what follows below. If two hydrogen ions participate in the oxidation-reduction electrode reaction, then on increasing the hydrogen ion concentration 17 times the rate of the cathodic reduction of ferrocyanide should increase 290 times [5]. If we compare the velocity of the processes to which Curves 2 and 3, Fig. 3 correspond at a potential e.g. of 0.5 V, then in 1 M sulfuric acid (by extrapolation of Curve 2, i.e., in the absence of concentration polarization) the process is speeded up approximately 300 times as compared with the process in 0.05 M sulfuric acid, in which the amount of free H^+ ions is 1/17th of that in 1 M solution. Thus, the kinetic relations also confirm the hypothesis of the participation of $H_2Fe(CN)_6^{2-}$ ions in the potentiometric reaction.

We shall now consider the effect of aluminum ions on the character of the potentiometric curves on the one hand, and on the kinetics of the electrode reaction on the other.

The experiments which we carried out on the potentiometric titration of zinc in the presence of aluminum salts (Fig. 7) showed that aluminum salts actually interfere with the titration since they smooth out the potential jumps at the equivalence point, their effect being greater the higher their concentration. Polarization curves for the system $Fe(CN)_6^{3-}$ – $H_2Fe(CN)_6^{2-}$ in the presence of aluminum salts at a concentration of 0.16 M (Curve 2, Fig. 5) almost fuse with the curves taken in the absence of these salts (Curve 3, Fig. 5). This indicates that the aluminum salts at a given concentration in practice do not impede the electrochemical reaction on the electrode; otherwise the overvoltage of the cathodic reduction process of the $Fe(CN)_6^{3-}$ ions in the presence of aluminum salts would be considerably greater. At a concentration of 0.54 M for the aluminum salt a fair degree of interference is observed, particularly for small negative charges on the platinum surface, at potentials of 0.25-0.05 V (Fig. 5, curve 1). Nevertheless, at the potentials in which we are interested and which are near to the equilibrium potentials for the system $Fe(CN)_6^{3-}$ to $H_2Fe(CN)_6^{2-}$, no essential slowing down is observed even for large concentrations of aluminum ions.

On the basis of these experiments it may be concluded that the anomaly observed in the potentiometric titration curves (Fig. 7) cannot be explained by the slowing down of the electrode reaction, but is caused apparently by chemical interaction of aluminum ions with ferrocyanide ions, leading to the formation of soluble but practically nondissociating aluminum ferrocyanide $Al_4[Fe(CN)_6]_3$. Actually, the equilibrium-reduction potential of the solution shifts to the positive side on increasing the concentration of aluminum salts, which indicates a decrease in the activity of the reducing ion $Fe(CN)_6^{4-}$. Moreover, on combining the aluminum into the stable oxalate complex, the titration curve acquires a normal shape (Curve 4, Fig. 7); the distortion observed (Curves 2 and 3, Fig. 7) is completely eliminated. Thus, the reason why aluminum affects the behavior of the electrode system ferricyanide-ferrocyanide has not been correctly explained hitherto.

The facts adduced above show that the slowness of the titration processes with ferrocyanide and the distortion of the shape of the potentiometric curve for all the conditions examined are related to difficulties of chemical reaction in solution, and not to the electrode reaction, which takes place rapidly enough in the cases considered.

The study of the reaction kinetics in the present work serves as a theoretical basis for the potentiometric methods worked out by us for the determination of zinc in magnesium [4] and aluminum alloys [11].

SUMMARY

1. By taking polarization curves (overvoltage curves) and by determining potential changes with time, the kinetics of the establishment of oxidation-reduction potentials in the system $Fe(CN)_6^{3-} - H_2Fe(CN)_6^{2-}$ on a platinum electrode has been studied.

2. The time required for the equilibrium to be established as calculated from the polarization curves, and also the potential changes with time, determined directly, showed that the potential in the system is established rapidly (in the course of seconds), so that the slowness of the potentiometric titration process (tens of minutes) cannot be the result of the slowness of the electrode reaction.

3. On the basis of direct potentiometric titration under different conditions it has been shown that the slowness of the titration process is related to the unfavorable course of chemical reactions in solution.

4. It has been shown that the factor which increases the rate of titration of zinc with ferrocyanide is the presence of H^+ and K^+ ions in solution, and a mechanism is advanced for the accelerating action of these ions.

5. Polarization measurements which were carried out showed the error of the viewpoint current in the literature that large amounts of aluminum salts desensitize the platinum electrode during titration with ferrocyanide ions, i.e., that the aluminum ions hinder the oxidation-reduction electrochemical reaction on the electrode. The influence of aluminum ions can apparently be attributed to their chemical interaction with ferrocyanide ions, leading to the formation of the soluble but practically non-dissociating compound $Al_4[Fe(CN)_6]_3$ aluminum ferrocyanide.

Combining aluminum into an oxalate complex destroys the distortion of the potentiometric titration curves.

6. In considering the effect of sulfuric acid on the polarization curves, it has been shown, in agreement with published material, that the electrochemical reaction on the platinum electrode in strongly acid solutions of ferrocyanide in which hydrogen ions participate proceeds according to the following scheme

$$2H^+ + Fe(CN)_6^{3-} + e \longrightarrow H_2Fe(CN)_6^{2-},$$

and not by the scheme

$$Fe(CN)_6^{3-} + e \longrightarrow Fe(CN)_6^{4-},$$

while the electrode potential is determined by the equation

$$\epsilon = \epsilon_0 + \frac{RT}{F} \ln \frac{[Fe(CN)_6^{3-}][H^+]^2}{[H_2Fe(CN)_6^{2-}]} .$$

7. The method adopted by the authors for taking and analyzing polarization curves as applied to the system $Fe(CN)_6^{3-} - H_2Fe(CN)_6^{2-}$, is a suitable method for studying the rate of a number of electrode reactions, in particular those which occur during potentiometric analysis.

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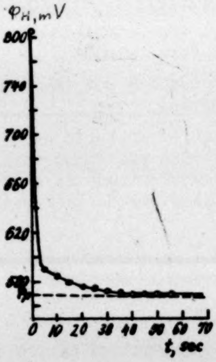

Fig. 9. Experimental curve for potential changes of the platinum electrode with time in the system $Fe(CN)_6^{3-} - Fe(CN)_6^{4-}$: $K_3Fe(CN)_6 = 1 \cdot 10^{-5}$ M; $K_4Fe(CN)_6 = 1 \cdot 10^{-5}$ M; $H_2SO_4 = 0.05$ M.

EXTRACTION OF MOLYBDENUM FROM HYDROCHLORIC ACID SOLUTIONS BY MEANS OF ETHER

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The use of organic solvents in extraction techniques for various metal complexes in order to determine the metals quantitatively is continuously gaining greater importance in analytical chemistry.

Many methods have appeared in recent years for separating the most varied compounds of the elements by extraction techniques involving organic reagents. Despite the undoubted practical interest of extraction methods and their application to the separation of inorganic compounds, insufficient interest has been displayed in the separation of inorganic complex compounds by extraction.

A quantitative separation of certain metals directly from an acid solution immediately after an aliquot has been dissolved is particularly attractive. In this connection the extraction of the chloride complexes of heavy metals during alloy analysis is of particular interest.

Although the extraction of several metallic chlorides especially ferric chloride has been used for a long time in analytical practice, the results given in the literature re the completeness of the extraction of chloride by ether and by other organic extractors under varying conditions [1,2,3] (See Table 1) are not full enough. In this connection it is probably the chloride of iron [1,4] and gallium [5], which have been studied in greatest detail.

TABLE 1

Extraction of various complex chlorides from hydrochloric acid solution by means of ether [1]

Element	Valency	Extracted (%)	Element	Valency	Extracted (%)
Vanadium	IV	Traces	Tin	IV	17
"	V	"	"	II	15-30
Gallium	III	97	Platinum	IV	Traces
Germanium	IV	40-60	Mercury	II	0.2
Iron	III	99	Selenium	IV	Traces
Gold	III	95	Antimony	III	6
Indium	III	Traces	"	V	81
Iridium	IV	5	Thalium	III	90-95
Copper	II	0.05	Tellurium	IV	34
Molybdenum	VI	80-90	Phosphorus	V	Traces
Arsenic	III	68	Zinc	II	0.2
"	V	2-4			

According to the scant published material [1,3] the chloride complex of molybdenum is extracted to a fair extent. We accordingly carried out experiments in which we studied the completeness of ether extractions for the molybdenum chloride complex at various hydrochloric acid concentrations in order to find the optimum conditions for the quantitative separation of molybdenum from other chlorides whose chlorides are not extracted by ether.

EXPERIMENTAL

The starting material was $(NH_4)_2MoO_4$ prepared by recrystallization of the paramolybdate from alcohol. Using this material, a solution was made in which the molybdenum content was determined gravimetrically by precipitation as lead molybdate. Molybdenum chloride was extracted at various hydrochloric acid concentrations. In each case ether saturated with the same strength of hydrochloric acid as in the aqueous solutions was used. In all cases the same volume of aqueous solutions (50 ml) was extracted, using the same volume of ether saturated with hydrochloric acid at the same concentration as in the aqueous solution.

The amount of molybdenum extracted with ether and that remaining in aqueous solution was determined photocolorimetrically using the molybdenum-ammonium thiocyanate color [6].

The results thus obtained are adduced in Table 2 and Fig. 1.

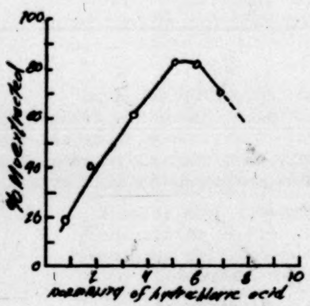

Fig. 1. Relation between % extraction of molybdenum and hydrochloric acid concentration (2 mg Mo in 50 ml).

The results show that optimum molybdenum extraction with ether is obtained from solution of 5-6 N acid; greater or lower acid concentrations lead to a decrease in the amount of molybdenum extracted from the aqueous solutions. This fact can be explained as follows. An increase in molybdenum extraction with increasing hydrochloric acid concentration is a consequence of a more complete formation of the complex acid $H[MoOCl_5]$ or $H[MoO_2Cl_3]$. On the other hand, an increase in hydrochloric acid concentration leads to greater solubility of ether in the aqueous phase, which in its turn affects the solubility of the complex compound in the aqueous phase. Thus 8% ether will dissolve in 0.9 N HCl, while in 1.7, 3.4, and 5.2 N HCl the solubilities of ether are 10, 12, and 19%, respectively. Measurements of the acidity of

TABLE 2

Percentage extraction of the chloride complex of molybdenum with ether

Concentration of HCl in the aqueous phase, (normality)	Mo taken in mg	Mo found in the aqueous layer in mg	% Mo extracted
0.9	2.00	1.62	19.0
1.7	2.00	1.19	40.5
3.4	2.00	0.78	61.0
5.2	2.00	0.31	84.5
6.0	2.00	0.34	83.0
6.9	2.00	0.57	71.5

the aqueous solution showed that the amount of acid before and after extraction remains practically unchanged.

It is of interest to note that maximum extraction of the chloride complexes of iron and gallium also occurs at approximately the same acid concentration.

There are indications in the literature [7], that certain chlorides, e.g., NH_4Cl, $CaCl_2$, and $AlCl_3$, increase the percentage of molybdenum extracted. Our work showed that the addition of these salts did not have any essential effect on the extraction of molybdenum from hydrochloric acid solutions by ether.

In order to determine how the completeness of the extraction of molybdenum depends on the number of extractions, repeated extractions were made of the same solution under optimum conditions (5.2 N HCl) (See Table 3).

TABLE 3

Extraction of the molybdenum chloride complex after repeated extractions

No. of extractions	Mo extracted (%)	% of original Mo extracted
1	84.5	84.5
2	78.0	96.0
3	70.3	99.0
4	~70.0	~99.5

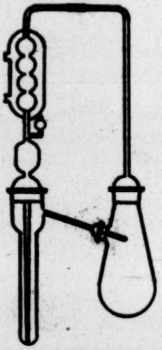

Fig. 2. Apparatus for automatic extraction with ether.

Extractions were carried out both by extraction in the usual separating funnels by shaking, and in a special automatic apparatus. During work with separating funnels the relation between percentage extraction and time of shaking was checked. Shaking was done for 1.5 and 10 minutes, there was no difference in the percentage extraction.

In order to extract the molybdenum chloride complex automatically the apparatus shown in Fig. 2 was used. This enabled extraction to be carried out with small amounts of ether (20-30 ml) in a comparatively short time. Thus 10 ml of a solution containing 2 mg molybdenum after extraction with ether saturated with hydrochloric acid gave a negative reaction with ammonium thiocyanate after 20 minutes.

The use of an automatic extraction apparatus enables one not only to economize on organic solvent but also to eliminate the operation of pouring the aqueous solution from one separating funnel to another during repeated extractions, this being an operation which is accompanied by loss of the extracted material. In addition, by working with the automatic apparatus, one can do without a fume chamber because the loss of extracting solvent is negligible.

SUMMARY

1. Experiments have shown that small amounts of molybdenum can be rapidly and quantitatively extracted from aqueous solution containing 5-6 N hydrochloric acid by means of ether. This enables molybdenum to be separated simply from a number of other elements whose chlorides are not extracted by ether.

2. It has been established that the percentage of molybdenum extracted depends to a considerable extent on the concentration of hydrochloric acid.

3. The use of an extraction apparatus cuts down the extraction time for molybdenum, increases the percentage extraction, and reduces the loss of extracted material to a minimum.

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THE APPLICATION OF THE ULTRAVIOLET IN ANALYTICAL CHEMISTRY

4. THE COLORIMETRIC DETERMINATION OF BISMUTH IN THE PRESENCE OF LARGE AMOUNTS OF LEAD

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One of the basic requirements of the methods normally used for the colorimetric determination of bismuth is the absence of lead in the test solution. This applies to such methods of determining bismuth as those involving its determination as its iodide complex [1], as colloidal bismuth sulfide, and also as the quinine or cinchonine salts with the iodide complex of bismuth. The method in which bismuth is determined as its complex with thiourea [2], although it enables determinations to be carried out in the presence of lead, nevertheless requires a knowledge of the amount of lead present, since the latter affects the bismuth calibration curve. Determination of bismuth in the presence of lead as its thiocyanate complex [3], is complicated by the fact that colorimetric determinations are carried out in sulfuric acid media. Other heavy metals in addition to lead interfere with bismuth determinations.

In the present work the difference in the behavior of the complex compounds of bismuth and lead with potassium bromide with respect to absorption of rays of wave length $\lambda = 365$ mμ is used as a basis for colorimetric determination of bismuth in the presence of lead.

Bismuth was determined using a photometer adapted for ultraviolet work [4]. The light source was a mercury high pressure lamp, the PRK-4. Ultraviolet radiation of $\lambda = 365$ mμ was isolated by means of a UFS-3 light filter. In order to determine the absorption of the 365 mμ ultraviolet radiation by the test solution, a fluorescent screen, the photoluminescence of which was excited by light of the given wave length, was used. The amount of ultraviolet absorption was measured by photocolorimetric comparison of the intensities of the photoluminescence of the two halves of the photometer field. The photoluminescence of one half was excited by the ultraviolet radiation passing through the solvent (water in this case), while the other half was excited by that passing through the solution. Comparison of both halves was made by means of a stop, the drum of which was graduated in terms of optical density.

Using a Beckmann spectrophotometer we got absorption curves for lead acetate in 1.45 M potassium bromide and for bismuth chloride in 0.53 M potassium bromide. The absorption curves obtained (Fig. 1) coincide very well with the curves obtained by Fromherz and Kun-Hoy-Lih [5], and Schaefer and Hein [6]. From these absorption curves it is obvious that at $\lambda = 365$ mμ, the complex of bismuth with potassium bromide has a maximum absorption, the absorption coefficient being high enough for carrying out sensitive colorimetric determinations of bismuth. The absorption of the given line ($\lambda = 365$ mμ) by the complex formed between lead and potassium bromide is insignificant.

Solutions of bismuth chloride and lead chloride and a saturated solution of potassium bromide in the cold (4.41 M) were used.

The effect of various amounts of potassium bromide on the absorption of the bismuth complex was checked first. Potassium bromide itself does not exhibit any absorption in the region $\lambda = 365$ mμ; its maximum absorption ($\log K_{max} = 4.04$) is located at $\lambda_{max} = 195$ mμ [7]. The results obtained for two different bismuth concentrations for various amounts of potassium bromide are represented in Fig. 2, where it can be seen that in order to get maximum absorption for the bismuth complex a concentration of 0.4 M potassium bromide in the test solution is sufficient; an excess of potassium bromide at the above concentration has no effect.

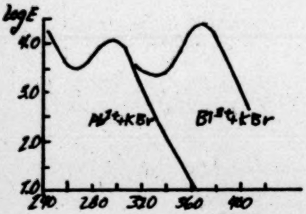

Fig. 1. Absorption curves for the ions Pb^{2+} + KBr and Bi^{3+} + KBr.

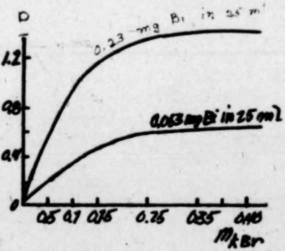

Fig. 2. Effect of potassium bromide on the absorption of the bismuth complex.

Experiments carried out in order to fix the concentration of potassium bromide necessary to give maximum absorption for the lead complex showed that increasing the concentration of potassium bromide up to the point where the solution is saturated with it in the cold leads to an ever increasing absorption by the complex, i.e., in order to get maximum absorption by the complex a large excess of potassium bromide is necessary. This indicates a greater stability for the bismuth complex as compared with the lead complex, and favorably affects the determination of bismuth in the presence of lead.1)

Subsequently the effect of hydrochloric acid and chlorides on the absorption of the bismuth complex was studied. Hydrochloric acid itself does exhibit ultraviolet absorption at $\lambda = 365$ mμ. The maximum absorption of the hydrated chloride ion lies at $\lambda = 181$ mμ [7]. Bismuth however readily forms complex chlorides with hydrochloric acid; it was essential, therefore, to check the effect of hydrochloric acid on the ultraviolet absorption of the bismuth complex with potassium bromide. Experiments were carried out with bismuth solutions in 0.5 M potassium bromide in which the hydrochloric acid concentration was varied. It was shown that increasing the concentration of hydrochloric acid to more than 0.2 N decreases the absorption of radiation of $\lambda = 365$ mμ by the test solution (see Table 1).

This is explained by the fact that bismuth forms a complex with hydrochloric acid which has a maximum absorption at $\lambda = 322$ mμ [6]. Schaefer and Hein explain this maximum by the formation of a complex compound $H_3[BiCl_6]$, the absorption of which is constant in 10-13 N hydrochloric acid.

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1) Experiments with the lead complex in potassium bromide were carried out in an ultraviolet photometer at $\lambda = 313$ mμ. The UFS-1 light filter was used in conjunction with a solution of potassium chromate. The fluorescing screen was excited by the rays of the given wave length.

TABLE 1

The effect of hydrochloric acid and chlorides on the absorption of the complex formed between bismuth and potassium bromide

Bi taken, in mg	Normality of HCl	Molarity of KBr	NH_4Cl (mg)	D
0.05	0.132	0.5	–	0.29
0.05	0.22	0.5	–	0.285
0.05	0.44	0.5	–	0.23
0.05	0.88	0.5	–	0.205
0.05	1.10	0.5	–	0.190
0.05	0.88	1.0	–	0.285
0.05	1.10	1.0	–	0.285
0.05	0.132	1.5	–	0.285
0.025	0.088	0.5	–	0.11
0.025	0.88	0.5	–	0.06
0.025	0.88	1.0	–	0.105
0.05	0.088	0.5	2.0	0.265
0.05	0.088	0.5	3.0	0.248
0.05	0.088	1.0	3.0	0.285

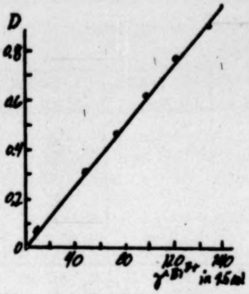

Fig. 3. Calibration curve.

As can be seen from this table, the effect of hydrochloric acid can be eliminated by the addition of larger amounts of potassium bromide (1-1.5 M solutions).

Chlorides showed a similar effect to hydrochloric acid.

By taking into account the necessary amount of potassium bromide as well as the permissible amount of hydrochloric acid, a calibration curve was constructed for the bismuth solutions (Fig. 3), which showed that a solution of bismuth-bromide complex follows Beer's law within the range of concentrations investigated (5-150 µg in 25 ml); within these concentration limits bismuth can be determined from the absorption in the ultraviolet.

First of all the amount of bismuth in solutions of known concentration was determined by means of the calibration curve (Table 2).

TABLE 2

Determination of the bismuth content from the calibration curve

Bi taken, in mg	Bi found, in mg	Relative error, %
0.020	0.0196	2.0
0.080	0.081	1.2
0.125	0.126	0.8

The results indicate that the method is accurate (the errors do not exceed 2%), and also has a high sensitivity.

Further investigations were carried out using the calibration curve adduced.

Determination of Bismuth in the Presence of Lead.

To a solution of bismuth salt of known concentration (100-25 µg Bi) contained in a 25 ml standard flask was added a solution of a lead salt (1-20 mg lead) acidified with hydrochloric acid, potassium bromide solution was then added so that its concentration in the final solution was approximately 1 M,[1] the solution being made up to the mark with distilled water. The solution was carefully mixed and placed in a quartz photometer cuvette with plane parallel sides (cuvette thickness 3 cm) and its optical density determined. Bismuth was then determined from the calibration curve. The results are given in Table 3.

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[1] Excess potassium bromide was necessary because lead was introduced as the chloride.

TABLE 3

Determination of bismuth in the presence of lead

Bi taken, in mg	Pb taken, in mg	Bi found, in mg	Error, in mg
0.100	1.0	0.100	–
0.100	2.0	0.102	+0.002
0.100	5.0	0.100	–
0.100	20.0	0.105	+0.005
0.060	4.0	0.060	–
0.060	10.0	0.059	–0.001
0.060	20.0	0.064	+0.004
0.025	10.0	0.025	–
0.025	20.0	0.029	+0.004

From Table 3 it follows that the presence of up to 20 mg of lead in 25 ml does not affect the bismuth determination. For the amount of bismuth determined this corresponds to a ratio of Bi:Pb of 1:2,000. If bismuth has to be determined in the presence of even greater amounts of lead, the latter can be removed as the chloride by simple evaporation of the solution. Experiments carried out for checking whether bismuth is coprecipitated with lead chloride showed that all the bismuth (as far as can be shown colorimetrically) remains in solution. The experiments were carried out as follows: 50 ml of solution containing a large amount of lead chloride (100-500 mg) and 50 μg Bi was acidified with 0.5 ml hydrochloric acid (1:1) and evaporated on a sand bath to a volume of 10-15 ml. The precipitate of lead chloride was filtered off and washed with a few milliliters of water acidified with hydrochloric acid. The filtrate was transferred to a standard flask (25 ml), potassium bromide added, and the optical density determined on a photometer. The results are given in Table 4 (Experiments Nos. 1-4).

TABLE 4

Determination of bismuth after partial removal of lead

Expt. No.	Bi taken, in mg	Pb taken, in mg	Bi found, in mg	Error, in mg
1	0.05	100.0	0.053	+0.003
2	0.05	200.0	0.058	+0.008
3	0.05	300.0	0.050	–
4	0.05	500.0	0.055	+0.005
5	0.020	500.0	0.019	–0.001
6	0.040	500.0	0.038	–0.002
7	0.040	500.0	0.040	–

Apart from the separation of large amounts of lead as the chloride we also checked on the possibility of determining bismuth colorimetrically with potassium bromide, preliminarily separating it with partially precipitated basic lead carbonate as suggested in 1949 by A. I. Busev and N. P. Korets [8].

To the acid solution containing lead and traces of bismuth 2N sodium carbonate solution was added until a small amount of precipitate appeared. The precipitate was allowed to stand 1-2 minutes, filtered off, and dissolved in dilute hydrochloric acid (so that 25 ml of the final solution contained 0.5 ml HCl). The solution was transferred to a standard flask, potassium bromide solution added, and the optical density measured. The results adduced in Table 4 (Experiments 5-7) show that bismuth can be determined when it has been separated by this method.

The Effect of Certain Heavy Metals on the Determination of Bismuth.

The effect of certain heavy elements in the determination of bismuth was also studied. The method of determination remained unchanged.

Determination of bismuth in the presence of copper showed that even in amounts of 2 mg/25 ml, the copper increases the results for bismuth. In order to eliminate the effect of copper it was reduced with ascorbic acid. Bivalent copper in solution as free ions is not reducible by ascorbic acid, but when bound as a complex ion (in our case with the bromide ions) it is easily reduced. Copper reduced by ascorbic acid does not interfere with bismuth determinations even in amounts up to 15 mg/25 ml (Table 5).

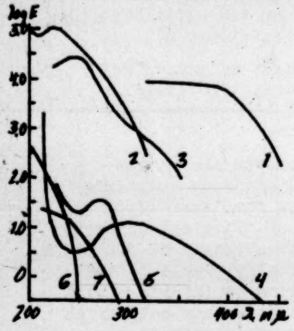

Fig. 4. Absorption curves. 1) $[FeBr]^{2+}$ ions; 2) $[HgBr_4]^{2-}$ ions; 3) $[SnBr_4]^{2-}$ ions; 4) $CuBr_2$ in KBr; 5) CuBr in KBr; 6) H_2SO_4; 7) Fe^{2+} ions.

The difference between the absorption curves for the complex of bivalent and univalent copper with the bromide ions can be readily seen from Fig. 4 [9]. The absorption curve for ascorbic acid is given in Fig. 5 [10].

Iron (III) forms a complex with bromide ions, the absorption curve for which has been given by Rabinowitsch and Stockmayer [11], and is also given in Fig. 4. From the absorption curve for the $FeBr^{2+}$ ions it is obvious that iron will interfere strongly with bismuth determinations. Nevertheless bismuth can still be determined in the presence of iron up to 20 mg iron /25 ml if the iron is reduced by ascorbic acid first, when it should not interfere. The absorption curve for Fe is given in Fig. 4 [12]. Results of the determination of bismuth in the presence of iron are given in Table 6. Moreover, when iron is present in large amounts it can be used as a collector for bismuth [13], in such a case iron is precipitated as hydroxide, the hydroxide is then dissolved in hydrochloric acid, and the iron is reduced with ascorbic acid.

With Br^- ions zinc and cadmium form complex anions, the maximum absorption of which lies in the far ultra-violet. For $[CdBr_4]^{2-}$ $\lambda_{max} = 227$ mμ while for $[ZnI_4]^{2-}$ $\lambda_{max} = 221$ mμ [7], and for the Br^- complex the maximum shifts even farther into the ultra-violet. Zinc and cadmium should not therefore interfere with bismuth determination. We showed (Table 6) experimentally that these elements even in amounts up to 50 mg/25 ml do not interfere with bismuth determinations.

TABLE 5

Determination of bismuth in the presence of copper

Bi taken, in mg	Cu taken, in mg	Bi found, in mg	Error, in mg	Observation
0.100	1.0	0.100	–	
0.100	2.0	0.105	+0.005	
0.050	2.0	0.055	+0.005	Without reduction
0.050	4.0	0.060	+0.010	
0.100	5.0	0.105	+0.005	
0.100	10.0	0.103	+0.003	
0.100	15.0	0.107	+0.007	
0.050	10.0	0.053	+0.003	After reduction
0.050	15.0	0.055	+0.005	with ascorbic acid
0.050	20.0	0.061	+0.011	

Mercury (II) forms complexes with bromides, the absorption curve of which is shown in Fig. 4 [14]. It is clear from the absorption curve that mercury should not interfere with bismuth determination. This was confirmed experimentally (Table 6): 10 mg of mercury in 25 ml of solution did not interfere.

Tin (II) reacts with a saturated solution of potassium bromide to give a complex, the absorption curve of which is given in Fig. 4 [15]. From this curve it is evident that tin should not interfere strongly with bismuth determinations. It was shown that 10 mg of tin (IV) or tin (II) in 25 ml of solution does not interfere with bismuth determination (Table 6).

Arsenic does not give stable compounds with bromide anions. The absorption curves for quinquevalent and trivalent arsenic are given in Fig. 5 [16]. It was shown that arsenic in amounts of 10 mg/25 ml does interfere with the bismuth determination (Table 6).

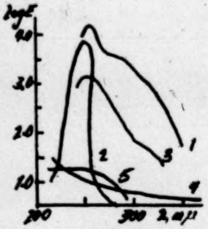

Fig. 5. Absorption curves. 1) Sb^{3+} ions; 2) ascorbic acid; 3) Sb^{5+} ions; 4) As^{3+} ions; 5) As^{5+} ions.

Antimony (III) absorbs the ultraviolet (Fig. 5) [17]. Antimony both tri- and quinquevalent forms complexes with bromides; the complex of trivalent antimony absorbs the ultraviolet strongly at $\lambda = 365$ mμ. It was shown experimentally (Table 6) that trivalent antimony begins to interfere with bismuth determinations at concentrations of 0.6 mg/25 ml. If, however, potassium tartrate is added to the test solution, the antimony can be complexed as a more stable tartrate which does not absorb the ultraviolet at $\lambda = 365$ mμ. When this is done antimony (III) in amounts of 3 mg/25 ml can be tolerated. Antimony (V) does not interfere in amounts of 20 mg/ 25 ml (Table 6).

The effect of nitric acid on the determination of bismuth was also checked. It is known [7], that nitric acid does not absorb the ultraviolet at $\lambda = 365$ mμ. The absorption spectrum of the hydrated NO_3^- ion consists of two maxima; one at 193.6 mμ (log $\epsilon_{max} = 4.08$) and a weak maximum at 302 mμ (log $\epsilon_{max} = 0.8-0.9$). It was shown experimentally (Table 6) that at nitric acid concentrations up to 0.5 N, correct results could be obtained for bismuth, but at higher concentrations the values for the bismuth content are too high. This is explicable by the partial decomposition of nitric acid under the action of the ultraviolet, as a result of which NO_2 is formed in solution, and this can absorb the ultraviolet strongly.

Sulfuric acid does not interfere (Fig. 4) [18].

None of the heavy metals tested, therefore, interfere strongly with the determination of bismuth by this method.

The method developed for the determination of bismuth in lead by using potassium bromide in the ultraviolet was checked on two samples of lead. Spectrographic analysis of the samples gave the following results. (See bottom of page 305).

TABLE 6

Determination of bismuth in the presence of heavy metals

Amounts taken, in mg											N_{HNO_3}	Found Bi, in mg
Bi	Fe	Zn	Cd	Hg	Sn (II)	Sn (IV)	As (III)	As (V)	Sb (III)	Sb (V)		
0.100	5.0											0.100
0.100	10.0											0.101
0.100	20.0											0.100
0.020	–	32.7										0.021
0.040	–	16.35										0.0382
0.040	–	49.04										0.0415
0.020	–	–	50.0									0.0415
0.040	–	–	50.0									0.040
0.040	–	–	–	5.0								0.0405
0.040	–	–	–	10.0								0.0405
0.020	–	–	–	5.0								0.0205
0.020	–	–	–	10.0								0.022
0.050	–	–	–	–	11.9							0.0523
0.100	–	–	–	–	19.8							0.1078
0.050	–	–	–	–	–	9.3						0.0523
0.050	–	–	–	–	–	18.6						0.060
0.020	–	–	–	–	–	–	15.0					0.020
0.020	–	–	–	–	–	–	30.0					0.022
0.050	–	–	–	–	–	–	15.0					0.052
0.050	–	–	–	–	–	–	22.5					0.059
0.020	–	–	–	–	–	–	–	9.0				0.019
0.020	–	–	–	–	–	–	–	15.0				0.021
0.050	–	–	–	–	–	–	–	–	0.63	With-		0.052
0.050	–	–	–	–	–	–	–	–	0.94	out		0.065
									tartaric acid			
0.050	–	–	–	–	–	–	–	–	3.14	With		0.0525
0.050	–	–	–	–	–	–	–	–	6.28	tar-		0.0528
									taric	acid		
0.020	–	–	–	–	–	–	–	–	–	19.0		0.0525
0.020	–	–	–	–	–	–	–	–	–	31.3		0.0580
0.040	–	–	–	–	–	–	–	–	–	–	0.28	0.0382
0.040	–	–	–	–	–	–	–	–	–	–	0.56	0.040
0.040	–	–	–	–	–	–	–	–	–	–	0.84	0.046
0.040	–	–	–	–	–	–	–	–	–	–	1.40	0.052

Elements	Sample No. 1	Sample No. 2
Pb	Main element	Main element
Sn	None	1-3%
Bi	0.01%	0.015%
Sb	None	0.015%
Ag	0.001%	traces
Si	0.0001%	–
Mg	0.001%	none
Fe	0.01%	traces
Cu	0.01%	0.0015%
As	–	0.001%

TABLE 7

Analysis of lead samples

No. of analysis	Sample No. 1			Sample No. 2		
	Pb taken, in mg	Bi found, in mg	% Bi	Pb taken, in mg	Bi found, in mg	% Bi
1	514.1	0.046	0.0089	-	-	-
2	584.9	0.050	0.0086	521.0	0.073	0.0140
3	505.6	0.043	0.0085	490.1	0.058	0.0118
4	522.7	0.047	0.0090	534.5	0.075	0.0140

Results for the colorimetric analysis of bismuth in the ultraviolet are given in Table 7.

An aliquot of the test material (0.5 g) was dissolved by heating in nitric acid (1:2). The analysis was then carried out as follows.

5 mg of ferric chloride was added to the nitric acid solution of the sample, the solution was heated and ammonia added dropwise till ferric hydroxide, which acts as a collector for the bismuth, was precipitated. The ferric hydroxide containing the bismuth was filtered off, washed with hot water, and then dissolved in dilute hydrochloric acid (1 ml of the concentrated acid in the final volume of 50 ml). The solution was transferred to a standard flask, the potassium bromide and ascorbic acid added, and the optical density of the solution determined. The results of experiments carried out using this technique are given in Table 7 under numbers 1 and 2.

The results given opposite No. 3 in Table 7 were obtained by coprecipitation of bismuth with lead sulfide, obtained by partial precipitation with hydrogen sulfide from hydrochloric acid solution. The sulfides were dissolved in strong hydrochloric acid and the analysis carried out as described above. All the results are close to those obtained by other methods; the method described however, is not so convenient, since colloidal sulfur, which strongly absorbs the ultraviolet including radiation of $\lambda = 365$ mμ, remains in the solution to be colorimetrically analyzed. It is necessary, therefore, to measure the optical density of the solution resulting from absorption by sulfur before adding the potassium bromide, then introducing the necessary correction; this lowers the accuracy of the results.

The results given in Table 7 opposite No. 4 were obtained without coprecipitation. The nitric acid solution was evaporated with hydrochloric acid to 20-25 ml. The lead dichloride which precipitated was filtered off and washed with water acidified with hydrochloric acid. The filtrate was transferred to a standard flask, potassium bromide and ascorbic acid added, and the optical density of the solution determined.

The preparation of solutions for determination of bismuth in the presence of large amounts of lead can thus be carried out by any of the analytical techniques which we have tested. The least accurate is the hydrogen sulfide method.

I should like to express my sincere thanks to Prof. Yuri Vitalevich Morachevsky for advice in carrying out the work.

SUMMARY

1. A colorimetric method is proposed for the determination of bismuth in the presence of large amounts of lead, which is based on the difference in absorption of the bromide complexes of bismuth and lead in the ultraviolet at $\lambda = 365$ mμ.

2. This method has been shown to possess a high sensitivity (0.2 μg Bi^{3+}/ml) and selectivity. The mean error is 1-2%.

3. The effect of heavy metals on the determination of bismuth (copper, iron, zinc, cadmium, mercury, tin, arsenic, and antimony) has been checked, and it has been established that bismuth can be determined in the presence of considerable amounts of these elements when this method is used.

4. The proposed method has been checked by using it for the determination of bismuth in two samples of metallic lead.

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1) See Consultants Bureau Translation, p. 35, ff.

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THE EFFECT OF HYDROGEN ION CONCENTRATION ON THE FORMATION OF INDIUM DITHIZONATE

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Methods involving the use of dithizone (diphenylthiocarbazone, $C_6H_5NHNHCSNC_6H_5$) in chemical analysis for the determination of many metals, both individually and in synthetic and natural mixtures, have been described in more than 100 papers published in the periodical literature. Nevertheless, in the case of certain metals, not only has no method been worked out for their determination by means of dithizone, but there is practically no information at all which characterizes the conditions of formation of the respective dithizonates. This is particularly true in the case of indium. There is only one indication that indium dithizonate can be extracted with carbon tetrachloride from aqueous solution at a pH of 5-6. Cyanides in solution do not interfere with the extraction [1].

A. T. Pilipenko, on the basis of the value of the instability constant of indium dithizonate which he determined, has calculated that the pH of the aqueous solution for complete extraction of indium as the dithizonate by means of carbon tetrachloride should be of the order of 4-5 [2]. These results exhaust all the information available on indium dithizonate.

There are no satisfactory methods for the determination of indium (apart from a polarographic method) in the presence of other metals, particularly when, as usually happens, only micro amounts are involved. Of particular importance is the determination of indium in the presence of zinc and cadmium, since indium often accompanies these metals in ores and during the intermediate stages of production.

The formation of metal dithizonates and their extraction by the non-aqueous phase depends to a considerable extent on the composition of the hydrogenous solutions; the hydrogen ion concentration and the presence or absence of other materials.

In this article, results of investigations of the relation between the formation of indium dithizonate and the pH of the aqueous solution are communicated.

METHODS OF INVESTIGATION AND MATERIALS USED

Analysis by means of dithizone is usually carried out by shaking the test solutions with small amounts of a solution of dithizone in a non-aqueous solvent. The metal dithizone formed during this procedure dissolves in the non-aqueous solvent to give a characteristic color to the solution. Extraction is made from a solution whose pH has been adjusted to a definite value and which is kept constant by means of a buffer.

Since a reaction is possible between the components of a buffer mixture and indium ions (we showed, e.g., that in the presence of a buffer consisting of citric acid and disodium hydrogen phosphate, indium dithizonate is not formed), we carried out tests in the presence of buffers which do not appreciably affect the formation of the dithizonates, and also with unbuffered solutions.

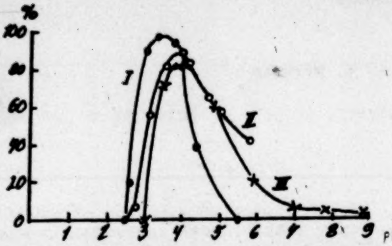

Fig. 1. Relation between extraction of indium dithizonate and pH during extraction titration with a carbon tetrachloride solution of dithizone. Curves: I) From unbuffered solutions; II) from solutions buffered with sodium acetate plus hydrochloric acid; III) from solutions buffered with acetic acid plus ammonia.

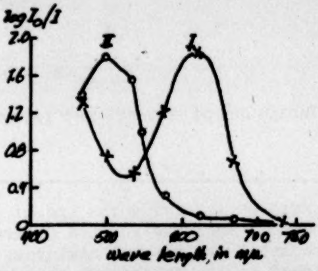

Fig. 2. Absorption curves for solutions of dithizone, I, and indium dithizonate, II, in carbon tetrachloride. Cuvette 10 mm.

We used mixtures of sodium acetate and hydrochloric acid, and of ammonia and acetic acid, as buffers. The pH of the unbuffered solutions was regulated by means of hydrochloric acid and ammonia solution. The pH was established potentiometrically.

In addition to normal purification all the materials were treated with dithizone. Dithizone was synthesized from phenylhydrazine hydrochloride [3], and was purified by treating its solution in chloroform with ammonia followed by precipitation with hydrochloric acid and then dissolving it in carbon tetrachloride. The working solution contained 3 mg dithizone/100 ml. Indium trichloride was prepared by dissolving metallic indium in hydrochloric acid. The solution contained 0.002 g indium/liter.

EXPERIMENTAL RESULTS

Solutions of indium trichloride of a definite concentration (50 μg in 50 ml calculated as the metal) and of a definite pH, buffered and unbuffered, were treated with the solution of dithizone in carbon tetrachloride in a separating funnel. The dithizone solution was added at first in portions of 2-3 ml and the whole shaken thoroughly, when the green color of the dithizone solution had changed to the pure red color of indium dithizonate, the non-aqueous phase was removed. Extraction titration was reckoned to be complete when the green color of the last portion of the non-aqueous phase (0.5 ml) on shaking for several minutes did not change, or, acquired the mixed color of solutions of dithizone plus dithizonate.

In the table the volumes (in ml) of dithizone solution used at a given pH for extracting the dithizonate by extraction titration are shown opposite the appropriate pH values of the indium trichloride solutions.

Expt. No.	Unbuffered solutions		In the presence of HCl + CH_3COONa		In the presence of CH_3COOH and NH_4OH	
	pH	Volume of dithizone solution in ml	pH	Volume of dithizone solution in ml	pH	Volume of dithizone solution in ml
1	2.49	0	2.41	0	2.98	0
2	2.53	5	2.72	2	3.50	18.5
3	3.12	23	3.20	14.5	3.95	21.5
4	3.41	25	3.67	21	4.25	21.5
5	3.92	24	4.10	23	4.92	18
6	4.45	10	4.26	21.5	5.92	6
7	5.45	0	4.72	17	7.03	2
8	-	-	5.07	15	7.91	2
9	-	-	5.84	11	8.91	2

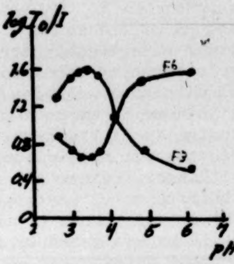

Fig. 3. Absorption curves for the non-aqueous phase in relation to the pH of the unbuffered indium trichloride solutions; F3) according to dithizone; F6) according to indium dithizonate.

The tabulated results show that maximum extraction of indium as the dithizonate from unbuffered solutions is observed at a pH of 3.4 (Experiment No. 4), while in the presence of acetate buffers the optimum pH is at 4.0-4.3 (Experiments Nos. 3,4, and 5). In order to construct a diagram from these results: percentage of indium extracted against pH, the completeness of the dithizonate extraction from unbuffered solutions was determined at pH of 3.4. To do this the solutions after extraction treatments with dithizone (25 ml of dithizone) were evaporated almost to dryness in a quartz beaker. The residue was treated with 2-3 ml of water, acidified with hydrochloric acid to a pH of 3.4. The solutions obtained were treated again with dithizone. Blank tests were also made at the same time. 1 ml of dithizone solution was required for the extraction of indium from the solution obtained after treatment of the dry residue, and 0.5 ml of dithizone solution for the blank.

Consequently, 1 µg of indium remained in 50 ml of solution after treatment with dithizone; this is equivalent to 98% extraction of indium under these conditions. Extraction of indium from a solution of pH 4.1 in the presence of a buffer mixture of sodium acetate and hydrochloric acid amounted to 90%, while in the presence of acetic acid and ammonia the extraction was 84%.

The tabulated results were calculated on the basis of the percentage indium extracted, assuming that for complete (100%) extraction from solution it would be necessary to use 25 ml dithizone solution. The results are given graphically in Fig. 1.

The curves in Fig. 1 differ from similar curves for the dithizonate of other metals; the curves for the latter usually, after reaching a maximum extraction for the dithizonate, remain at a constant level for a large pH range. The extraction of indium dithizonate differs in that it depends to a very considerable extent on the pH of the solution. At pH values greater or less than the optimum the percentage extraction of indium dithizonate decreases sharply, being particularly steep for unbuffered solutions. In order, therefore, to separate indium from other metals and in order to determine it quantitatively, extraction should be carried out from solutions whose pH corresponds to the optimum. The relation between indium dithizonate extraction and pH of the aqueous solution which is depicted in Fig. 1 was confirmed by other experiments carried out by another method. The indium trichloride solutions (of equal concentrations) were not treated with separate portions of dithizone solution as described above, but by simultaneous addition of dithizone in amounts greater than that necessary for complexing all the indium as dithizonate. Therefore, after shaking vigorously for several minutes the non-aqueous phase always contained a mixture of indium dithizonate and dithizone. Since all the solutions of indium trichloride independently of their pH were treated with equal volumes of a solution of dithizone, then the relation between the extraction of dithizonate and pH of the water phase could be estimated by the change in optical density of the aqueous phase. The optical density was measured on a Pulfrich refractometer using light filters Nos. 3 and 6 in a cuvette with a layer thickness of 10 mm.

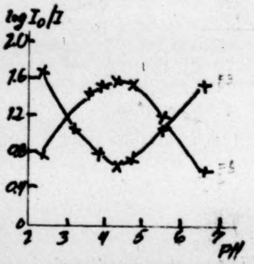

Fig. 4. Relation between light absorption curves for the non-aqueous phase and pH of the indium chloride solutions buffered with acetic acid and ammonia. F3) dithizone; F6) indium dithizonate.

The optical density of a dithizone solution in carbon tetrachloride is a maximum for light filter No. 3 with a transmission band at 598-639 mμ (effective wave length 619 mμ). The optical density of a solution of indium dithizonate is very small in this range and has hardly any effect on the value of the optical density of the dithizone solution, but has a maximum with light filter No. 6 with a transmission band at 476-516 mμ (effective wave length 496 mμ). In this region (light filter No. 6) however a dithizone solution equimolar in concentration with the indium dithizonate solution also possesses a considerable optical density (Fig. 2). Measurements of the optical density of the non-aqueous phase (solution of dithizone and dithizonate) was accordingly carried out as follows.

The optical density was measured first using light filter No. 3. The optical density thus obtained corresponds to the concentration of unreacted dithizone. The non-aqueous phase was then freed from dithizone by carefully heating it with dilute ammonia solution until there was a change from the mixed color to pure red; then using light filter No. 6 the optical density of the indium dithizonate solution was measured.[1] The results given in Fig. 3 are for unbuffered solutions while those in Fig. 4 are for solutions buffered with ammonia and acetic acid. Curves F3 and F6 were taken using light filters Nos. 3 and 6, and show the relation between changes in optical density of the non-aqueous phases and pH of the aqueous solution of indium chloride, according to the dithizone which has not reacted with indium – F3, and according to the dithizonate extracted from the aqueous phase – F6.

The position of the minimum and maximum on these curves corresponds to maximum extraction of dithizonate and agrees very well with the position of

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1) Indium dithizonate, like a number of other dithizonates, is decomposed by aqueous ammonia. When, however, a mixture of dithizone and indium dithizonate

(continued on next page)

the maximum on the curves in Fig. 1 (as compared with curve III, Fig. 1, the positions of the maximum and minimum on the curve in Fig. 4 are shifted to the right by 0.1-0.2 pH units).

As far as the stability of the indium dithizonate solution in carbon tetrachloride is concerned, it was shown that it did not decompose on treating it with weakly acidified water (pH >3) and the buffer mixture mentioned above (pH >4). This is illustrated in Fig. 5. 10 ml of acidified water or the same volume of a buffer mixture were shaken in separating funnels with individual portions of the indium dithizonate solution in carbon tetrachloride[1]. After the red color of the non-aqueous phase had turned green (decomposition of the dithizonate) the non-aqueous phase was removed and a new portion of dithizonate solution introduced. This treatment was stopped when the last portion of non-aqueous phase kept the color of the indium dithizonate solution (decomposition has ceased) after shaking.

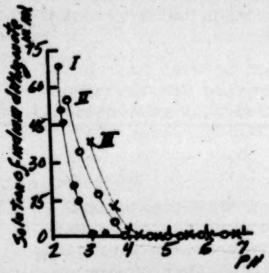

Fig. 5. Decomposition curves for solutions of indium dithizonate in carbon tetrachloride: I) Water acidified with hydrochloric acid: II) buffered with sodium acetate plus hydrochloric acid; III) buffered with ammonia plus acetic acid.

The volumes of dithizonate solution decomposed at various pH's are plotted along the ordinate (Fig. 5) while pH is plotted along the abscissa.

A consideration of Figs. 1 and 5 enables one to assume that equilibrium in the system: dithizone (in carbon tetrachloride) - indium salt (in aqueous solution) is established within a measurable time interval.

The course of the reaction between dithizone and indium in relation to the time of contact between the aqueous and non-aqueous phases for a 20% excess of dithizone and for a pH of 5.62 of the aqueous solution (buffer mixture of acetic acid and ammonia) is shown in Fig. 6. The course of the reaction was controlled by measurements of the optical density of the non-aqueous phase using light filters Nos. 3 and 6. It follows from Fig. 6 that the equilibrium discussed above is established after approximately 6 hours (measurements in the course of 6 to 24 hours showed that the optical density of the non-aqueous phase does not change).

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in carbon tetrachloride is treated with a dilute ammonia solution, decomposition of the dithizonate is only observed after all the dithizone has switched over from the non-aqueous to the aqueous phase. If the ammonia solution is diluted in the ratio 1:1000 (2000), then on continued treatment, the decomposition of dithizonate is so insignificant that there is practically no difference in the optical density of the non-aqueous phase.

[1] The indium dithizonate solution was made by shaking a solution of dithizone (3 mg dithizone in 100 ml carbon tetrachloride) with a solution of indium chloride in such excess that the green color of the non-aqueous phase changes to the pure red of the dithizonate solution.

At the optimum pH and also for lower pH values of the aqueous solutions, equilibrium was established more rapidly; in unbuffered solutions – within the time taken to carry out extraction titration.

At the optimum pH and also for lower pH values of the aqueous solutions, equilibrium was established more rapidly; in unbuffered solutions – within the time taken to carry out extraction titration.

The relation between extraction of indium dithizonate and the pH of solutions buffered with acetic acid and ammonia for a 20% excess of dithizone and a phase contact time of 17 hours was investigated.

It was found that the optimum pH value under these conditions was the same as for extraction titration; in contrast to the latter, however, a complete (100%) extraction of indium into the non-aqueous phase (Fig. 7) was realized. For comparison, curve III which was obtained during extraction titration in the presence of acetic acid and ammonia (Fig. 1) is also given in Fig. 7.

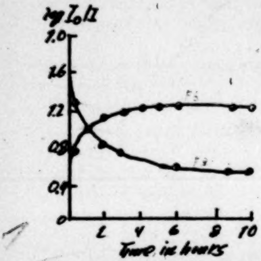

Fig. 6. Light absorption curves for the non-aqueous phase in relation to the time of contact between a carbon tetrachloride solution and the aqueous solution of indium chloride, buffered with a mixture of ammonia and acetic acid (pH 5.62): F3) according to the dithizone, F6) according to the indium dithizonate.

When extraction was made from unbuffered solutions and a long contact time allowed between the phases, the range in which extraction with indium could be carried out was somewhat wider than during extraction titration, mainly on the high pH side.

Determination of Indium in the Presence of Other Metals

The characteristic relation between indium dithizonate extraction and pH of the aqueous solution, particularly during extraction titration, distinguishes the behavior of the dithizonate from the dithizonates of other metals. This fact enables one in certain simple cases to extract indium from other metals accompanying it, simply by regulating the pH of the aqueous solution, there being no need of a complexing agent.

In this way it is possible to separate metals whose dithizonates precipitate at pH's less than 2.5.

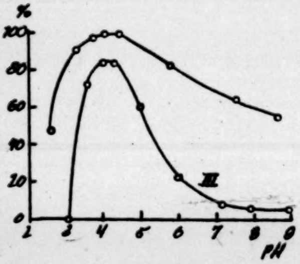

Fig. 7. The relation between indium dithizonate extraction and the pH of solutions buffered with a mixture of ammonia and acetic acid, for a 20% excess of dithizone and a time of contact between the phases of 17 hours. Curve III) for extraction titration.

Palladium, gold, platinum, mercury, silver and copper belong to this group. Since the dithizonates of these metals shift into the non-aqueous phase in the sequence given, then, e.g. if both palladium and copper are present simultaneously, more palladium than copper will react with dithizone.

Experiments on the separation of copper and mercury at pH 1-2 with a concentration ratio of In:Cu(Hg) varying from 0.01 to 100 showed that copper and mercury go over into the non-aqueous phase (CCl_4) completely in the form of dithizonates, while all the indium remains in the aqueous phase. On increasing the pH to 3.5 or 4.0-4.4 (buffer mixture) the indium concentration was determined easily and accurately.

As a result of the sequence for separation of the dithizonates given above, one can assume that other metals of this group (palladium, gold, platinum, and silver) can also be readily separated from indium.

In all probability neither will metals whose dithizonates can only be extracted from neutral or alkaline solutions (cobalt, nickel, lead, univalent thallium) interfere with the direct determination of indium. The direct determination of indium is, however, complicated in the presence of metals whose dithizonates start to precipitate at pH's of 2.5-6.7.

Thus, the separation of indium from zinc or cadmium is only possible when their concentrations are of the same order (e.g. 50 μg each in 50 ml). Separation can be effected in this case if the zinc and cadmium are separated first at a pH of 7-7.5 (by means of paranitro phenol). Under these conditions all the indium remains in solution. In practice, the concentrations of these metals in a test solution are almost invariably greater than the indium concentration.

If the zinc or cadmium concentration is considerably greater than that of indium in our experiments Zn(Cd):In varied from 16 to 100, then it is impossible to separate them by regulating the pH. At pH 6-9 indium is partially precipitated with zinc and cadmium. At pH 3.5 a considerable amount of zinc and cadmium are extracted with indium.

It is known that bismuth, tin and trivalent thallium will be extracted with indium (whatever the concentration), since the dithizonates of these metals are formed at the same pH as indium dithizonate (initial separation at pH 2-4).

In cases of this type where it is necessary to separate indium, complexing agents must be added to the solution in addition to controlling the pH.

SUMMARY

1. The extraction of indium dithizonate from aqueous solutions of indium trichloride by means of a solution of dithizone in carbon tetrachloride depends to a considerable extent on the pH of the aqueous solutions (the pH's must be accurately controlled), and also on the contact time between the aqueous and non-aqueous phases, and excess dithizone.

2. Maximum indium dithizonate extraction from solutions containing acetate buffer mixtures is observed at a pH of 4-4.3, while from unbuffered solutions optimum extraction is observed at a pH of 3.5.

3. The extraction of indium is more complete than in extraction titration for a long contact time between the aqueous solution of indium trichloride and the non-aqueous dithizone solution and for an excess of the latter.

4. Copper, mercury, palladium, gold, platinum, silver, and small amounts of zinc and cadmium can be completely separated from indium without using complexing agents.

5. Cobalt, nickel, lead and univalent thallium should not interfere with indium determinations.

6. Indium cannot be separated from bismuth, tin, trivalent thallium and relatively large amounts of zinc and cadmium simply by controlling the pH; in addition it is necessary to add complexing agents which will complex the metals or the indium into compounds which do not react with dithizone.

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THE ANALYTICAL APPLICATION OF DIPHENYLTHIOCARBAZONE (DITHIZONE)

IV. THE INSTABILITY CONSTANTS OF THE DITHIZONATES OF NICKEL, COBALT, TIN (II), BISMUTH, COPPER (II), SILVER, MERCURY (II), AND THE DITHIZONATES OF MANGANESE AND IRON

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The acidic properties of dithizone have been considered previously [1], and results have been given of determinations of the instability constants of the dithizonates of zinc, cadmium, lead [2], thallium and indium [3]. In the present article results are given on the determinations of the composition and instability constants of the dithizonates of nickel, cobalt, tin, bismuth, copper, silver, mercury, manganese, and iron.

Composition of the Dithizonates of Nickel, Cobalt, Tin (II), Bismuth, Copper (II), Silver, Mercury (II), Manganese, and Iron

In order to study the composition of the dithizonates of nickel, cobalt, tin (II), bismuth, copper (II), mercury (II), and silver, diagrams of composition-light absorption were studied as in previous work [4]. The experiments were carried out as follows.

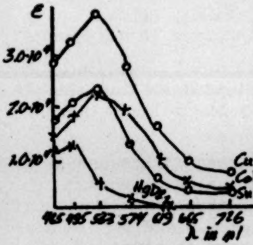

Fig. 1.

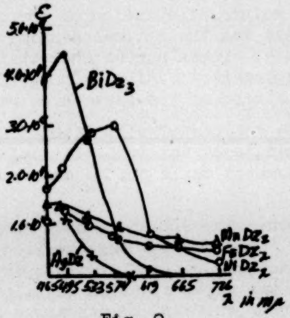

Fig. 2.

Equimolecular solutions of both dithizone and metal salt respectively were prepared, viz a 10^{-4}M solution of dithizone in CCl_4 and a 10^{-4}M solution of the metal salts in water. These solutions were mixed in various proportions so that the total volume was a constant. After shaking, the CCl_4 layer was removed, diluted to a definite volume (10 ml) with carbon tetrachloride and the optical density (D) of the solution measured on an FM photometer. While studying the composition of the dithizonates of copper, mercury, and silver a small amount of 0.1 N sulfuric acid was added to the solutions, since the composition of these dithizonates in acid and alkaline solution varies. When the composition of the other dithizonates was studied, suitable buffer mixtures were added.

In order to choose the appropriate light filters, absorption curves for solutions of the dithizonates of nickel, cobalt, tin (II), bismuth, copper (II), silver, mercury (II), iron (II) and manganese were studied on an FM photometer; these curves are adduced in Figs. 1 and 2. Wave length in millimicrons is plotted on the abscissa, while light absorption by solutions of the respective dithizonates in carbon tetrachloride is expressed by the molar absorption coefficient along the ordinate.

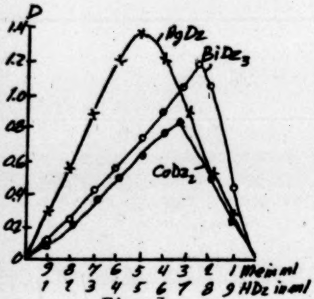

Fig. 3.

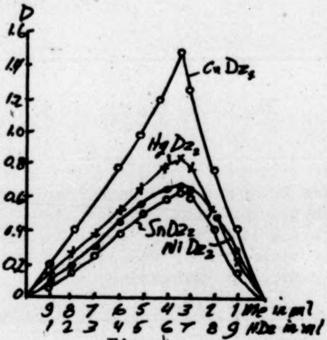

Fig. 4.

Results for the determination of the composition of the dithizonates of nickel, cobalt, tin (II), copper (II), silver, and mercury (II) are adduced in Figs. 3 and 4. The ratio of the volume of 10^{-4}M solution of dithizone (in CCl_4) to the volume of solution of the metal salt (in water) is plotted along the abscissa and the optical density of the solutions on the ordinate in Figs. 3 and 4. These curves show that the maxima correspond to compositions for the complexes of: $NiDz_2$, $CoDz_2$, $SnDz_2$, $BiDz_3$, AgDz, $HgDz_2$ and $CuDz_2$. The composition of the last three was determined in acid media.

Iron (II) and manganese only react with dithizone at pH's > 7. Under these conditions however, manganese and iron are rapidly oxidized so that the composition of their dithizonates could not be determined by the method described above.

In order to determine the composition of iron and manganese dithizonates, respectively, the following technique was employed. A solution of known concentration of dithizone in CCl_4 was prepared and 10 ml of it placed in a separating funnel. To this was added a buffer solution of pH 8.6 and the respective solutions of ferrous sulfate and manganous sulfate also added. The latter were taken in large excess (100-200 excess). The contents of the separating funnel were shaken vigorously. The manganese and iron thereupon oxidized, but a part managed to react with dithizone. The solution was allowed to stand for some time before the non-aqueous layer was filtered through a dry filter for retention of any aqueous solution contained in the CCl_4; it was then evaporated, treated with nitric acid, and the iron and manganese finally determined colorimetrically (Table 1).

TABLE 1

Dithizone taken	Mn found (μg)	Corresponding amt. of 10^{-3}M solution of manganese in ml	Ratio Mn^{2+}:HDz	Dithizone taken	Fe taken (μg)	Corresponding amt. of 10^{-3}M solution of iron in ml	Ratio Fe:HDz
10 ml $2\cdot10^{-4}$ M/1	0.062	1.1	1.1:2	10 ml $2\cdot10^{-4}$ M/1	0.057	1.0	1:2
20 ml $2\cdot10^{-4}$ M/1	0.121	2.2	1.1:2	20 ml $2\cdot10^{-4}$ M/1	0.119	1.1	1.1:2
5 ml $2\cdot10^{-3}$ M/1	0.33	6.0	1.2:2	5 ml $2\cdot10^{-3}$ M/1	0.31	5.5	1.1:2
10 ml $2\cdot10^{-3}$ M/1	0.59	10.7	1.1:2	10 ml $2\cdot10^{-3}$ M/1	0.63	11.5	1.1:2

The results given in Table 1 show that the composition of manganese and iron dithizonates corresponds to a ratio of metal to dithizone of 1:2.

The Instability Constants of the Dithizonates of Nickel, Cobalt, Tin, Bismuth, and Copper.

In order to determine the instability constants of the dithizonates of these metals, as before, we studied [2,3], the equilibrium reactions for the formation of dithizonates in relation to the pH of the aqueous phase, the concentration of dithizone in CCl_4, and of the metal salt in water. Equation (1) was used for the experimental determination of the value of the constants of bivalent metal dithizonates:

$$\frac{[M^{2+}]_{H_2O}\cdot[HDz]^2_{CCl_4}\cdot(K'_{HDz})^2}{[MDz_2]_{CCl_4}\cdot[H^+]^2_{H_2O}} = K'_{MDz_2}, \qquad (1)$$

while for the trivalent metal dithizonates, equation (2) was used:

$$\frac{[M^{3+}]_{H_2O}\cdot[HDz]^3_{CCl_4}\cdot(K'_{HDz})^3}{[MDz_3]_{CCl_4}\cdot[H^+]^3_{H_2O}} = K'_{MDz_3}, \qquad (2)$$

where $[M^{2+}]_{H_2O}$ and $[M^{3+}]_{H_2O}$ are metal ion concentrations in water; $[HDz]_{CCl_4}$, $[MDz_2]_{CCl_4}$ and $[MDz_3]_{CCl_4}$ are the respective concentrations of dithizone and dithizonate in CCl_4; $[H^+]_{H_2O}$ is the hydrogen ion concentration in the water; and $K'_{HDz} = 2\cdot10^{-9}$ [1].

Method of Determination and Results

To a separating funnel was added a known volume of acetate-ammonia buffer solution in the case of nickel, cobalt, and tin, while a known volume of standard sulfuric acid was used for bismuth and copper. The values for the hydrogen ion concentration of the test solutions are given in column 1 of Tables 2-6. 5 ml of a 10^{-4}M solution of metal salt was then added, followed by water to bring the mixture up to a standard volume. In the case of nickel, cobalt, and tin, 5 ml of a $2\cdot10^{-4}$M solution of dithizone in CCl_4 was then added, while in the case of bismuth 5 ml of a $3\cdot10^{-4}$M solution of dithizone in CCl_4 was added, and for the determination of the instability constant of copper dithizonate 10 ml of 10^{-4}M dithizone solution was used.

After shaking and when the layers had separated out, the CCl_4 layer was removed and the amount of dithizonate formed determined colorimetrically by a method described previously [2]. The values of the instability constants of the dithizonate complexes were calculated by means of formulas (1) and (2)

TABLE 2

pH	Nickel dithizonate found, in millimoles	Equilibrium Concentrations			K'_{NiDz}
		$[Ni^{2+}]$ in H_2O phase, $[M^{2+}]$ in M	[HDz] in CCl_4 phase, in M	$[NiDz_2]$ in CCl_4, phase, M	
5.1	$3.8 \cdot 10^{-4}$	$1.2 \cdot 10^{-5}$	$0.48 \cdot 10^{-4}$	$0.76 \cdot 10^{-4}$	$2.3 \cdot 10^{-17}$
5.7	$4.6 \cdot 10^{-4}$	$0.4 \cdot 10^{-5}$	$0.16 \cdot 10^{-4}$	$0.92 \cdot 10^{-4}$	$1.1 \cdot 10^{-17}$
6.45	$4.9 \cdot 10^{-4}$	$0.1 \cdot 10^{-5}$	$0.04 \cdot 10^{-4}$	$0.98 \cdot 10^{-4}$	$0.5 \cdot 10^{-17}$
6.4	$4.8 \cdot 10^{-4}$	$0.2 \cdot 10^{-5}$	$0.08 \cdot 10^{-4}$	$0.96 \cdot 10^{-4}$	$3.3 \cdot 10^{-17}$
6.7	$4.9 \cdot 10^{-4}$	$0.1 \cdot 10^{-5}$	$0.04 \cdot 10^{-4}$	$0.98 \cdot 10^{-4}$	$1.6 \cdot 10^{-17}$
4.6	$2.8 \cdot 10^{-4}$	$2.2 \cdot 10^{-5}$	$0.88 \cdot 10^{-4}$	$0.44 \cdot 10^{-4}$	$1.5 \cdot 10^{-17}$
				Mean	$1.7 \cdot 10^{-17}$

TABLE 3

pH	Cobalt dithizonate found in millimoles	Equilibrium Concentrations			K'_{CoDz_2}
		$[Cd^{2+}]$ in H_2O phase, in M	[HDz] in CCl_4 phase, in M	$[CoDz_2]$ in CCl_4 phase, in M	
4.93	4.25	$0.75 \cdot 10^{-5}$	$0.30 \cdot 10^{-4}$	$0.85 \cdot 10^{-4}$	$2.3 \cdot 10^{-18}$
4.62	3.35	$1.65 \cdot 10^{-5}$	$0.66 \cdot 10^{-4}$	$0.67 \cdot 10^{-4}$	$7.6 \cdot 10^{-18}$
4.05	1.95	$3.05 \cdot 10^{-5}$	$1.22 \cdot 10^{-4}$	$0.39 \cdot 10^{-4}$	$5.9 \cdot 10^{-18}$
3.95	1.75	$3.25 \cdot 10^{-5}$	$1.30 \cdot 10^{-4}$	$0.35 \cdot 10^{-4}$	$5.4 \cdot 10^{-18}$
3.96	1.60	$3.40 \cdot 10^{-5}$	$1.36 \cdot 10^{-4}$	$0.32 \cdot 10^{-4}$	$3.9 \cdot 10^{-18}$
3.68	0.85	$4.05 \cdot 10^{-5}$	$1.62 \cdot 10^{-4}$	$0.19 \cdot 10^{-4}$	$5.1 \cdot 10^{-18}$
				Mean	5.10^{-18}

TABLE 4

pH	Tin dithizonate found in millimoles	Equilibrium Concentrations			K'_{SnDz_2}
		$[Sn^{2+}]$ in H_2O phase, in M	[HDz] in CCl_4 phase, in M	$[SnDz_2]$ in CCl_4 phase, in M	
5.4	3.3	$1.7 \cdot 10^{-5}$	$0.68 \cdot 10^{-4}$	$0.66 \cdot 10^{-4}$	$3.4 \cdot 10^{-16}$
6.0	4.1	$0.9 \cdot 10^{-5}$	$0.36 \cdot 10^{-4}$	$0.82 \cdot 10^{-4}$	$5.8 \cdot 10^{-16}$
6.1	4.25	$0.75 \cdot 10^{-5}$	$0.30 \cdot 10^{-4}$	$0.85 \cdot 10^{-4}$	$5.0 \cdot 10^{-16}$
6.2	4.35	$0.65 \cdot 10^{-5}$	$0.26 \cdot 10^{-4}$	$0.87 \cdot 10^{-4}$	$3.2 \cdot 10^{-16}$
6.4	4.75	$0.25 \cdot 10^{-5}$	$0.10 \cdot 10^{-4}$	$0.95 \cdot 10^{-4}$	$5.3 \cdot 10^{-16}$
4.9	1.6	$3.4 \cdot 10^{-5}$	$1.36 \cdot 10^{-4}$	$0.32 \cdot 10^{-4}$	$5.0 \cdot 10^{-16}$
4.6	0.9	$4.1 \cdot 10^{-5}$	$1.64 \cdot 10^{-4}$	$0.18 \cdot 10^{-4}$	$3.9 \cdot 10^{-16}$
				Mean	$4.5 \cdot 10^{-16}$

from the experimental results. The results given in Tables 2, 3, 4, 5, and 6 are those obtained for the dithizonates of nickel, cobalt, tin, bismuth, and copper respectively.

The respective values of the instability constants were thus found to be: nickel $-1.7 \cdot 10^{-17}$; cobalt $-5 \cdot 10^{-18}$; tin $-4.5 \cdot 10^{-16}$, bismuth $-1.1 \cdot 10^{-37}$ and copper $-1.1 \cdot 10^{-27}$.

TABLE 5

$[H^+]$	Bismuth dithizonate found, in millimoles	Equilibrium Concentrations			K'_{BiDz_3}
		$[Bi^{3+}]$ in H_2O phase, in M	$[HDz]$ in CCl_4 phase, in M	$[BiDz_3]$ in CCl_4 phase, in M	
0.484	1.9	$3.1\cdot10^{-5}$	$1.56\cdot10^{-4}$	$0.38\cdot10^{-4}$	$2.2\cdot10^{-37}$
0.390	2.4	$2.6\cdot10^{-5}$	$1.26\cdot10^{-4}$	$0.48\cdot10^{-4}$	$1.5\cdot10^{-37}$
0.289	2.9	$2.1\cdot10^{-5}$	$0.96\cdot10^{-4}$	$0.58\cdot10^{-4}$	$1.1\cdot10^{-37}$
0.190	3.4	$1.6\cdot10^{-5}$	$0.66\cdot10^{-4}$	$0.68\cdot10^{-4}$	$0.8\cdot10^{-37}$
0.097	3.8	$1.2\cdot10^{-5}$	$0.42\cdot10^{-4}$	$0.76\cdot10^{-4}$	$1.0\cdot10^{-37}$
0.052	4.1	$0.9\cdot10^{-5}$	$0.24\cdot10^{-4}$	$0.82\cdot10^{-4}$	$0.9\cdot10^{-37}$
0.030	4.3	$0.7\cdot10^{-5}$	$0.12\cdot10^{-4}$	$0.86\cdot10^{-4}$	$0.4\cdot10^{-37}$
				Mean	$1.1\cdot10^{-37}$

TABLE 6

$[H^+]$	Copper dithizonate found, in millimoles	Equilibrium Concentrations			K'_{CuDz_2}
		$[Cu^{2+}]$ in H_2O phase, in M	$[HDz]$ in CCl_4 phase, in M	$[CuDz_2]$ in CCl_4 phase, in M	
3.66	2.1	$1.93\cdot10^{-5}$	$0.79\cdot10^{-4}$	$0.21\cdot10^{-4}$	$2.2\cdot10^{-27}$
4.0	2.4	$2.6\cdot10^{-5}$	$0.76\cdot10^{-4}$	$0.24\cdot10^{-4}$	$1.6\cdot10^{-27}$
5.0	2.25	$2.75\cdot10^{-5}$	$0.775\cdot10^{-4}$	$0.225\cdot10^{-4}$	$1.2\cdot10^{-27}$
4.66	2.15	$1.9\cdot10^{-5}$	$0.785\cdot10^{-4}$	$0.215\cdot10^{-4}$	$1.0\cdot10^{-27}$
6.66	1.85	$2.1\cdot10^{-5}$	$0.815\cdot10^{-4}$	$0.185\cdot10^{-4}$	$0.7\cdot10^{-27}$
7.5	1.75	$1.62\cdot10^{-5}$	$0.825\cdot10^{-4}$	$0.175\cdot10^{-4}$	$0.5\cdot10^{-27}$
8.0	1.45	$1.42\cdot10^{-5}$	$0.855\cdot10^{-4}$	$0.145\cdot10^{-4}$	$0.5\cdot10^{-27}$
				Mean	$1.1\cdot10^{-27}$

Determination of the Instability Constants of Mercury and Silver

Silver and mercury dithizonates are so stable that the ions of these metals can be combined with dithizone at any acidity. It has been shown experimentally that silver and mercury dithizonates dissolved in CCl_4 are not destroyed with 10 N sulfuric acid. There is consequently no chance of carrying out determinations using the concentration of the free metal ions. In order, therefore, to determine their instability constants the equilibrium reactionsbetween their dithizonates and halides were studied; the latter form stable compounds with mercury, but the silver halides have very slow solubility. The concentration of the halide ions and the acidity of the solution are thereupon changed. It should be possible to calculate the value of the instability constant of mercury dithizonate by means of equation (1), while that of silver dithizonate can be calculated from equation (3), which was derived previously [3]:

$$\frac{[M^+]_{H_2O}\cdot[HDz]_{CCl_4}\cdot K'_{HDz}}{[MDz]_{CCl_4}\cdot[H^+]_{H_2O}} = K'_{MDz}. \qquad (3)$$

There is,however, no possibility of determining the metal ion concentration experimentally. Since there is a complexing agent in the aqueous phase (halide ions), which was introduced to combine with the mercury and silver ions, then for the case of mercury in aqueous solution the following equation holds:

$$[H^{2+}] + 4X^- = HgX_4^{2-}, \tag{4}$$

or

$$\frac{[Hg^{2+}][X^-]^4}{[HgX_4^{2-}]} = K_{HgX_4^{2-}}, \tag{5}$$

from which

$$[Hg^{2+}] = \frac{K_{HgX_4^{2-}} \cdot [HgX_4^{2-}]}{[X^-]^4} \tag{6}$$

By substituting this value in equation (1) we get:

$$K'_{HgDz_2} = \frac{K_{HgX_4^{2-}} \cdot [HgX_4^{2-}]_{H_2O} \cdot [HDz]^2_{CCl_4} \cdot (K'_{HDz})^2}{[X^-]^4_{H_2O} \cdot [HgDz_2]_{CCl} \cdot [H^+]^2_{H_2O}} . \tag{7}$$

In the case of the formation of silver dithizonate in the presence of halide ions, the concentration of silver ions in the aqueous phase is determined by the equation:

$$[Ag^+] = \frac{Lp_{AgX}}{[X^-]_{H_2O}} . \tag{8}$$

Substituting this value in equation (3) we get:

$$K'_{AgDz} = \frac{Lp_{AgX} \cdot [HDz]_{CCl_4} \cdot K'_{HDz}}{[X^-]_{H_2O} \cdot [H^+]_{H_2O} \cdot [AgDz]_{CCl_4}} . \tag{9}$$

Equations (7) and (9) can be conveniently used for calculating the instability constants of mercury and silver from the experimental results.

TABLE 7

Vol. 10 N H_2SO_4 in ml	Vol. of 1 M halide, in ml	Vol. H_2O phase, in ml	Halide used	Equilibrium Concentrations in moles/l.					K'_{HgDz_2}
				$[HgDz_2]$ in CCl_4 phase	$[HDz]$ in CCl_4 phase	$[HgX_4^{2-}]$ in H_2O phase	$[H^+]$ in H_2O phase	$[X^-]$ in H_2O phase	
0.2	0.02	10.2	I^-	$0.315 \cdot 10^{-4}$	$0.37 \cdot 10^{-4}$	$0.18 \cdot 10^{-4}$	0.196	$1.93 \cdot 10^{-3}$	$0.30 \cdot 10^{-44}$
0.5	0.02	10.0	I^-	$0.225 \cdot 10^{-4}$	$0.55 \cdot 10^{-4}$	$0.275 \cdot 10^{-4}$	0.5	$1.89 \cdot 10^{-3}$	$0.25 \cdot 10^{-44}$
1.0	0.01	10.0	I^-	$0.225 \cdot 10^{-4}$	$0.55 \cdot 10^{-4}$	$0.275 \cdot 10^{-4}$	1.0	$0.89 \cdot 10^{-3}$	$1.20 \cdot 10^{-44}$
1.0	2.0	10.0	Br^-	$0.220 \cdot 10^{-4}$	$0.56 \cdot 10^{-4}$	$0.28 \cdot 10^{-4}$	1.0	0.2	$0.23 \cdot 10^{-44}$
1.0	1.0	10.0	Br^-	$0.30 \cdot 10^{-4}$	$0.40 \cdot 10^{-4}$	$0.20 \cdot 10^{-4}$	1.0	0.1	$0.98 \cdot 10^{-44}$
0.5	4.0	10.0	Br^-	$0.13 \cdot 10^{-4}$	$0.74 \cdot 10^{-4}$	$0.37 \cdot 10^{-4}$	0.5	0.4	$0.22 \cdot 10^{-44}$
0.5	10.5	16.0	Br^-	$0.03 \cdot 10^{-4}$	$0.94 \cdot 10^{-4}$	$0.47 \cdot 10^{-4}$	0.312	0.66	$0.69 \cdot 10^{-44}$
8.0	6.0	15.0	Cl^-	$0.36 \cdot 10^{-4}$	$0.28 \cdot 10^{-4}$	$0.09 \cdot 10^{-4}$	5.33	0.4	$0.63 \cdot 10^{-44}$
6.0	9.0	20.0	Cl^-	$0.34 \cdot 10^{-4}$	$0.32 \cdot 10^{-4}$	$0.08 \cdot 10^{-4}$	3.0	0.45	$0.29 \cdot 10^{-44}$
4.0	15.0	15.0	Cl^-	$0.34 \cdot 10^{-4}$	$0.32 \cdot 10^{-4}$	$0.11 \cdot 10^{-4}$	2.66	1.0	$2.01 \cdot 10^{-44}$
								Mean	$0.68 \cdot 10^{-44}$

Experimental Technique

The following procedure was adopted for the determination of the instability constant of mercury dithizonate. A known volume of 10 N sulfuric acid was placed in a separating funnel and 5 ml of 10^{-4} M mercuric nitrate solution added; a known volume of halide was then added and the mixture made up to standard volume with water as indicated in column 3, Table 7. 10 ml of 10^{-4} M solution of dithizone in CCl_4 was finally added. The volumes of 10 N sulfuric acid and 1 M potassium

TABLE 8

Vol. 10 N H_2SO_4, in ml	Vol. 1 M potassium halide	Vol. H_2O phase, in ml	Halide used	Equilibrium Concentrations (M/l)				K'_{AgDz}
				[AgDz] in CCl_4 phase	[HDz] in CCl_4 phase	$[X^-]$ in CCl_4 phase	$[H^+]$ in H_2O phase	
1.0	0.05	11.05	Br^-	$0.18 \cdot 10^{-4}$	$0.82 \cdot 10^{-4}$	0.005	0.9	$0.8 \cdot 10^{-18}$
0.2	0.05	10.25	Br^-	$0.16 \cdot 10^{-4}$	$0.84 \cdot 10^{-4}$	0.005	0.2	$4.2 \cdot 10^{-18}$
0.05	0.05	10.1	Br^-	$0.40 \cdot 10^{-4}$	$0.60 \cdot 10^{-4}$	0.005	0.05	$4.8 \cdot 10^{-18}$
0.4	0.02	10.0	Br^-	$0.35 \cdot 10^{-4}$	$0.65 \cdot 10^{-4}$	0.002	0.4	$1.9 \cdot 10^{-18}$
0.1	0.1	10.0	Br^-	$0.25 \cdot 10^{-4}$	$0.75 \cdot 10^{-4}$	0.01	0.1	$2.4 \cdot 10^{-18}$
1.0	1.0	20.0	Cl^-	$0.34 \cdot 10^{-4}$	$0.64 \cdot 10^{-4}$	0.15	0.5	$1.1 \cdot 10^{-18}$
0.5	0.5	20.0	Cl^-	$0.74 \cdot 10^{-4}$	$0.26 \cdot 10^{-4}$	0.075	0.25	$0.8 \cdot 10^{-18}$
0.5	2.0	20.0	Cl^-	$0.30 \cdot 10^{-4}$	$0.70 \cdot 10^{-4}$	0.30	0.25	$1.4 \cdot 10^{-18}$
0.2	5.0	20.0	Cl^-	$0.26 \cdot 10^{-4}$	$0.74 \cdot 10^{-4}$	0.75	0.10	$1.6 \cdot 10^{-18}$
0.1	4.0	20.0	Cl^-	$0.28 \cdot 10^{-4}$	$0.72 \cdot 10^{-4}$	0.60	0.05	$3.6 \cdot 10^{-18}$
							Mean	$2.3 \cdot 10^{-18}$

halide solution used are given in columns 1 and 2 of Table 7. After shaking, and when the layers had separated, the CCl_4 layer was removed and 0.5-1 ml of 1 N sulfuric acid and 10 ml of 10^{-4}M silver nitrate added to it; the whole was then shaken up and the CCl_4 layer again separated and the excess silver nitrate determined by titration with dithizone. Using these results, the equilibrium concentrations of mercury dithizonate and mercury halide were calculated; these values are adduced in columns 5,6 and 7 of Table 7. Columns 8, 4 and 9 of the same table contain hydrogen ion concentrations, the complexing agent used, and its concentration, respectively. In the case of potassium chloride, 3 M solution was used; the table however, contains the values calculated for 1 M solution. Column 10 contains the calculated values of the instability constants of mercury dithizonate, in which equation (7) was used for calculating from the experimental results. The values for the instability constants of the halide complexes used [5], were: $K_{HgI_4} = 5.3 \cdot 10^{-31}$; $K_{HgBr_4} = 2.3 \cdot 10^{-22}$; $K_{HgCl_4} = 1.1 \cdot 10^{-16}$.

The instability constant of silver dithizonate was determined in the same way as that of mercury dithizonate, equation (9) being used for calculating from the experimental results.

The experimental results and the calculated values of the instability constant of silver dithizonate are given in Table 8. The data given in Table 8 is as follows: Column 1 – the volume of 10 N sulfuric acid used, in ml; column 2 – volume of 1 M halide solution; column 3 – volume of the aqueous phase; column 4 – the halide used; all these refer to the respective values used for calculating the instability constant of silver dithizonate. The equilibrium concentrations of silver dithizonate and of dithizone in CCl_4 are given in columns 5 and 6, while columns 7 and 8 contain the halide concentration and the hydrogen concentration in the water. The values obtained for the instability constant of silver dithizonate are given in column 9. The values for the respective solubility products used for calculation were [5], $Lp_{AgBr} = 4 \cdot 10^{-13}$ and $Lp_{AgCl} = 0.21 \cdot 10^{-12}$.

From Tables 7 and 8 the instability constant of mercury dithizonate has a value of $0.7 \cdot 10^{-44}$, while that of silver dithizonate is $2.3 \cdot 10^{-18}$, i.e., these compounds are so stable that it is necessary to increase the acidities of the solution and to add complexing agents such as halide ions, thiourea, etc., in order to disrupt them.

SUMMARY

1. The composition of the dithizonates of nickel, cobalt, tin (II), bismuth, copper (II), mercury (II) and silver has been studied by physico-chemico analysis of their solutions. The composition of manganese (II) and iron (II) dithizonates was determined from the results of chemical analysis of their dithizonates in CCl_4. It was found that the composition of silver dithizonate corresponds to the formula AgDz, of the dithizonates of bivalent metals to MDz_2 and of bismuth dithizonate to $BiDz_3$. In the case of copper, mercury, and silver the results adduced relate to dithizonates obtained in an acid medium.

2. Absorption curves for light by solutions of the dithizonates indicated in CCl_4 were studied.

3. Equilibrium between dithizone and the salts of nickel, cobalt, tin (II), bismuth, copper (II), mercury (II), and silver at various acid concentrations, and at various concentrations of the salts of these metals has been studied. The equilibrium between dithizone and mercury and silver salts was studied in the presence of halides. The instability constants of the dithizonates have been calculated on the basis of the experimental results. The values obtained were as follows:

$K'_{NiDz_2} = 1.7\cdot10^{-17}$; $K'_{CoDz_2} = 5\cdot10^{-18}$;

$K'_{BiDz_3} = 1.1\cdot10^{-37}$; $K'_{CuDz_2} = 1.1\cdot10^{-27}$;

$K'_{HgDz_2} = 0.7\cdot10^{-44}$ $K'_{AgDz} = 2.3\cdot10^{-18}$;

$K'_{SnDz_2} = 4.5\cdot10^{-18}$

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THE GRAVIMETRIC DETERMINATION OF LITHIUM

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Of the various methods used for the quantitative determination of lithium (gravimetric, volumetric, colorimetric, electrochemical, and spectrographic), the oldest, most numerous, and most often used are the gravimetric ones. These include determination of lithium as phosphate, sulfate, aluminate, and zinc uranyl acetate. The suggestions put forward in the literature that lithium can be determined gravimetrically as the carbonate [1], and even the chloride, can not be considered sound.

The phosphate method, which was suggested a long time ago by Berzelius [2] has evoked considerable attention and lively arguments and has been assessed several times. Some workers, such as Rammelsberg [3], Kraut, Nahnsen, and Cuno [4], reckon that the method gives high results; further, at a later date Rammelsberg [5], and Murmann [6], in general denied the possibility of getting lithium phosphate free from sodium. Other workers, e.g., Mayer [7], considered that the precipitation of lithium by means of secondary sodium phosphate in the presence of sodium hydroxide ensures that pure lithium phosphate is obtained by this precipitation. Merling [8], and Fresenius [9], also considered the method to be completely suitable. There is still no unanimity re this method.

The determination of lithium as the sulfate, which was worked out more than 100 years ago, continues to be the most widely used and apparently the most reliable method. If one does not take into account Carnot's method [10], according to which lithium is first of all separated from sodium and potassium by precipitation as the fluoride, all the remaining methods use differences in the solubilities of lithium chloride and the chlorides of the other alkali metals in organic solvents. Consequently, such methods assume that the alkali metals before determination must be converted into the chlorides. This group of methods can be subdivided into two. To the first group belong all gravimetric methods of determining lithium based on a preliminary treatment of the dry mixture of the alkali chlorides with organic solvents in order to extract the lithium chloride directly, the latter being then converted to sulfate. This group includes the methods of Rammelsberg [11], Kahlenberg and Krauskopf [12], Winkler [13], Brown and Reddy [14], and Sinka [15]. They differ mainly only in the solvents used for the extraction of lithium chloride from the other chlorides. Thus, Rammelsberg recommends an anhydrous mixture of ethyl alcohol and ether for extraction of lithium chloride; the mixture, however, does not give a good separation of lithium and sodium, while Kahlenberg and Krauskopf recommend as a solvent pyridine, which, unfortunately, has unpleasant physiological properties. Winkler used normal butyl alcohol; this alcohol, however, necessitates the introduction of appreciable corrections for the solubility of sodium and potassium chlorides. In a newer method, Brown and Reddy used acetone for extraction; unfortunately, lithium chloride is relatively only weakly soluble. Sinka recommended dioxane, which is specific, but is not readily available and is expensive. To the second group belong gravimetric methods based on a preliminary separation of sodium and potassium chlorides from a solution of all the chlorides by precipitation with organic reagents. This group includes the methods of Gooch [16], Palkin [17], and Caley and Axelrod [18].

Gooch's method, which in its original form was applied as an extraction process and was subsequently modified, found wide application, and, particularly in factory laboratories, is the most used for quantitative determination of lithium. Essentially, it consists of the dehydration of an aqueous solution of the mixed chlorides by means of an organic solvent with a high boiling point – isoamyl alcohol, which dissolves lithium chloride and precipitates sodium and potassium chlorides The serious drawback of this method is the physiological activity of isoamyl alcohol, and the necessity of applying corrections for the solubilities of sodium and potassium chlorides; moreover, these corrections depend on the other salts present in the mixture, so that it all leads to uncertainty. Before the correction can be applied, the volume of solvent after extraction has to be measured, and this is not always convenient.

Palkin's method is a variant of Rammelsberg's method: instead of dissolving the lithium chloride, it is recommended that sodium and potassium chlorides be precipitated from aqueous solution, in order to do which the concentrated aqueous solution of the chlorides is treated first with alcohol and then with ether The best results are obtained when the total weight of chlorides does not exceed 0.5 g. Caley and Axelrod's method is based on the same principle as Gooch's method, but they recommend the use of n-hexanol and 2-ethyl hexanol instead of isoamyl alcohol. Since these solvents for lithium chloride do not require the application of corrections for the solubilities of other alkali chlorides and have a high boiling point, they undoubtedly are the best solvents for the determination of lithium on the principle of this group of methods. Actually, Caley and Axelrod's method is good for the determination of small amounts of lithium chloride and for its separation from moderate amounts of sodium and potassium chlorides. However, as the result of the moderate solubility of lithium chloride in these solvents, the separation is not satisfactory for comparatively large amounts of lithium chloride, unless several extractions are made. A special position among this group of methods under consideration is occupied by Willand and Smith's suggestion [19], which is a combination of the types mentioned: according to their suggestion, lithium and sodium are first extracted from the mixed perchlorates of the alkali metals by means of n-butyl alcohol, while the sodium perchlorate is subsequently precipitated in the extract with a solution of 20% HCl in butyl alcohol. This method is rather complicated, and has not been used very much. Separation by means of fractional extraction and the composition of the extracting solvents for the separation of lithium have been described by Smith 20 .

Other, more recent methods for the gravimetric determination of lithium are precipitation as lithium aluminate and lithium zinc uranyl acetate. Precipitation as the aluminate was suggested by Grother and Savelsberg [21]. This method can scarcely be regarded as reliable, since the analytical results vary within a wide range. When determinations are carried out by this method, the pH must be adjusted and controlled carefully; precipitation cannot be regarded as complete under 60 hours; even then duplication of results is not always achieved. Precipitation of lithium as the zinc uranyl acetate, worked out by Gruttner [22], gives good results according to the author, for the determination of 0.6-10 mg of lithium in solution; the error, however, is greater than for determination of lithium as sulfate.

A similar method was proposed even earlier by Yu. A. Chernikhov, T.A Uspensky, and R.S.Aanaina [23], for the determination of small amounts of lithium in its alloys with magnesium. Unfortunately, the test samples have first of all to be purified from sodium salts,which are also precipitated by the reagent; for this purpose, extraction of anhydrous chlorides with isoamyl alcohol, which is the basis of Gooch's method, is recommended. In general, a return to non-aqueous solvents in methods involving separation of lithium and sodium from potassium, rubidium, and cesium is a characteristic trend. Thus, in a description of the chemical analysis of the alkali group of metals, Kato [24] recommends that after separation of lithium and sodium from potassium, rubidium, and cesium, the former should be converted into the chlorides, after which lithium is separated from sodium by the difference in the solubilities of their chlorides in amyl alcohol.

Describing a method for the analysis of silicates containing lithium and sodium, Miller [25], recommends isoamyl alcohol for the separation of lithium from mixtures of its chloride with the chlorides of sodium, potassium and calcium; he also recommends the use of acetone for solving the problem.

Hardly any new solvents have been suggested for use in the analysis of lithium in the last twenty years. The sole exception seems to be that of Caley and Axelrod which we have cited.

A review of the gravimetric methods for determination of lithium shows the leading part played by those methods which use the sulfate as the form to be determined gravimetrically and in which the most important part is the extraction processes. Further development of such methods should be based on a systematic study of the solubilities of the alkali chlorides in organic solvents, since previous investigations with their haphazard character may or may not lead the analyst to a successful method. Nevertheless, the material evidence already available shows that organic compounds which are good solvents for lithium chloride are also solvents for sodium and potassium chlorides to an appreciable extent; on the other hand, solvents which do not touch sodium and potassium chlorides do not dissolve lithium chloride to an extent sufficient for reliable extraction. It follows from what has been said that a reliable selective solvent has not yet been found, and there are no generalizations which can be used as a basis for a systematic search for such a solvent. This, of course, does not mean that we cannot immediately use some solvent or other for the separation of lithium compounds from the compounds of the other alkali elements by using their solubility characteristics.

EXPERIMENTAL

During a systematic study of the solubility of the chlorides of the alkali metals in saturated alcohols we focussed our attention on n-propyl alcohol as a solvent which is entirely suitable for extracting lithium chloride from a mixture of the other alkali chlorides. This solvent has not been previously used for extraction despite the fact that it possesses some essential advantages:

1) It is less physiologically active than all the alcohols, solvent mixtures and pyridine used previously.

2) It has a high solvent power for lithium chloride, its solvent power only being exceeded by ethyl and methyl alcohols, which dissolve appreciable amounts of the other chlorides.

At the same time, at normal temperature, the solubility of sodium and potassium chlorides in n-propyl alcohol is such that it creates a favorable ratio between their solubility and the solubility of lithium chloride which enables one under certain conditions to do away altogether with the application of corrections in quantitative determinations. A study of the true solubility of lithium, sodium, and potassium chlorides and the effects of solution time on the amount of chloride that goes into solution in n-propyl alcohol at 25° was carried out in the usual type of 80 ml flask immersed in a thermostat and provided with seals and mechanical stirrers. Temperature variation did not exceed ± 0.1°. Test samples were removed with a pipet fitted with a cotton filter and transferred to a vessel for weighing.

Lithium was then usually converted into the sulfate on the basis of whose weight the solubility in percent weight was determined. Some solubility determinations were made in parallel in which the chloride in solution was determined by Mohr's method. The results of the two series of experiments were in good agreement. Determination of the solubilities of sodium and potassium chloride were made by titration of the chloride solutions with 0.01 N silver nitrate by Mohr's method. When the Mohr method was used the chloride solutions were evaporated to remove organic solvent and the chloride determined in aqueous solution. In those cases where it was only possible to carry out qualitative tests, no titrations were made and only an estimate of the solubility of the salt was made by testing with silver nitrate. All the chlorides used were prepared from analytical grade chemicals by two-three recrystallizations. The purity of each chloride was checked by spectrographic analysis. The n-propyl alcohol from Schering had a boiling point of 97.2°.

The rate at which the chlorides of lithium, sodium and potassium dissolved in n-propyl alcohol at 25° is shown in Table 1, in which the solubilities are expressed in percent weight at various times from the beginning of the test.

TABLE 1

Chlorides	Solubility in % weight after					
	10 min.	20 min.	30 min.	60 min.	24 hrs.	6-7 days (equilibrium)
LiCl	11.78	12.63	14.05	14.41	14.52	15.60
NaCl	Traces	Traces	0.016	0.016	Not. determin.	0.019
KCl	None	None	Traces	0.007	" "	0.008

The tabulated results show that the equilibrium solubility of lithium chloride is more than 750 times that of sodium chloride and more than 1500 times that of potassium chloride. Another noteworthy feature is that most of the lithium chloride dissolves in the first 10-20 minutes, while a very insignificant amount of sodium chloride dissolves and none of the potassium chloride in the same time. This means that the solution rates of the individual chlorides in n-propyl alcohol are favorable for extraction for analytical purposes - the rates decrease from lithium to potassium chloride so that the difference in the amount of salts dissolving becomes even more favorable to the lithium chloride. In order to prevent any sodium or potassium chlorides dissolving in the solution during extraction of lithium chloride with n-propyl alcohol, we used alcohol which had been previously saturated with dry gaseous hydrogen chloride. We incidentally checked on the solubility of rubidium, cesium, and barium chlorides under these conditions. Table 2 contains results on the solubility of the chlorides of lithium, sodium, potassium, rubidium, cesium, and barium in n-propyl alcohol, saturated with gaseous hydrogen chloride at 25°. Solubility is expressed in percent weight in relation to the time for taking a sample from the moment when the test was started. The solubility of lithium chloride was determined by the sulfate method, the presence of the other chlorides in solution was checked by characteristic qualitative reactions; for sodium - reaction with zinc uranyl acetate; for potassium and rubidium - reaction with chloroplatinic acid and for cesium - reaction with sodium silicomolybdate.

TABLE 2

Chlorides	Solubility in % weight after		
	20 min.	60 min.	2 hours
LiCl	9.26	11.00	Not determin.
NaCl	None	None	None
KCl	"	"	"
RbCl	"	"	"
CsCl	"	"	"
$BaCl_2$	"	"	"

TABLE 3

Expt. No.	LiCl taken in g	NaCl taken in g	KCl taken in g	LiCl found in g	Error in LiCl in g
1	0.1030	–	–	0.1029	-0.0001
2	0.1085	–	–	0.1084	-0.0001
3	0.1178	–	–	0.1176	-0.0002
4	0.2527	–	–	0.2528	+0.0001
5	0.0442	0.2830	–	0.0440	-0.0002
6	0.1185	0.1049	–	0.1184	-0.0001
7	0.1280	0.1106	–	0.1284	+0.0004
8	0.1758	0.2089	–	0.1754	-0.0004
9	0.2351	0.2166	–	0.2354	+0.0003
10	0.2819	0.2519	–	0.2815	-0.0004
11	0.1814	–	0.1388	0.1815	+0.0001
12	0.0769	0.2284	0.2026	0.0769	±0.0000
13	0.1741	0.1045	0.0567	0.1738	-0.0003
14	0.2065	0.1591	0.1655	0.2067	+0.0002

It was thus shown that the alkali chlorides with the exception of lithium chloride, and of barium chloride for long extraction periods with n-propyl alcohol saturated with dry gaseous hydrogen chloride, do not dissolve in this alcohol.

Lithium chloride can therefore be determined; the solubility of lithium chloride, although slightly lower than in the pure solvent, is still high and exceeds the solubility of all other solvents recommended previously. Calcium must be removed.

Numerous experiments on extraction of lithium chloride from mixtures of its chloride with that of sodium and potassium chlorides confirmed that n-propyl alcohol saturated with dry, gaseous, hydrogen chloride can be used as a solvent. The results obtained for the determination of lithium after extraction as chloride and conversion into sulfate, and by the chloride ion are given in Table 3. In experiments 7-10 and 12-14 the residue after evaporation of the salt solution was treated with alcohol; in the others, lithium chloride or its mixtures with the other chlorides.

The results given in Table 3 show that by extraction of lithium chloride with n-propyl alcohol saturated with dry, gaseous, hydrogen chloride, it is possible to determine lithium as the sulfate in initial amounts of 40 mg to 0.3 g calculated as chloride, with very little error. We checked on the purity of the two lithium sulfate precipitates obtained after extraction of lithium chloride from the chloride mixtures; in both cases no sodium or potassium could be found spectrographically.

METHOD

0.8 g of the dry precipitate of the alkali chlorides was worked up in 15 ml of n-propyl alcohol saturated with dry, gaseous, hydrogen chloride, the salt crystals being carefully ground up for 3-5 minutes with a glass rod. The solution was left to stand for some time and then poured through a fine filter into a pure platinum or quartz beaker.

Experiment showed that when more than 0.15 g of lithium chloride was present in the mixture, one extraction was not enough (95-96% of lithium chloride was extracted during the first extraction) so that for accurate determinations it was necessary to repeat the extraction under the same conditions as the first. After the second extraction, the filter was treated in a separate beaker with 5 ml of solvent and the solution combined with the bulk of the extracted lithium chloride by passing it through the cleaned filter; beaker and filter were rinsed with two 5-ml lots of solvent and the wash solution combined with the rest. Treatment of the filter in a beaker is necessary because a very small amount of finely dispersed lithium chloride could, after the first extraction, pass together with the solution on to the filter and not be included in the second extraction involving treatment with the glass rod. The combined solution contained in the platinum or quartz beaker and containing all the lithium chloride was evaporated to a minimum volume on a sand bath and then transferred to a tared platinum or quartz crucible, where it was also evaporated. The beaker was rinsed with small amounts of distilled water and the wash water also added to the same crucible, after which the contents were evaporated to dryness. During evaporation of the solution in the beaker one must be careful to avoid complete evaporation, for in that case it would be difficult to wash off all the chloride from the beaker walls, as the solution would be too thick and its viscosity high.

The lithium chloride was converted into sulfate, which was then calcined at 650-700° in a muffle for 30 minutes and then weighed; calcining was repeated for 10-15 minutes to constant weight.

If small platinum or quartz beakers ca. 50 ml are available, it is more convenient to transfer the solution after extraction directly into the beaker, and to carry out evaporation and conversion into the sulfate in it.

SUMMARY

1. A brief review is given of published work on the gravimetric determination of lithium.

2. The solubility of lithium, sodium, and potassium chlorides in n-propyl alcohol at 25° has been studied.

3. It has been shown that lithium chloride can be extracted reliably from a mixture of the alkali chlorides by means of n-propyl alcohol saturated with dry aqueous hydrogen chloride.

4. A method is suggested for the quantitative determination of lithium as the sulfate based on the extraction of lithium chloride from a mixture of chlorides by means of n-propyl alcohol.

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THE DIRECT BROMATOMETRIC TITRATION OF BISMUTH, IRON, COPPER AND OTHER METAL HYDROXYQUINOLATES

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The methods most often used for the volumetric determination of metals with 8-hydroxyquinoline is that based on direct bromatometric titration [1]. KBr and a small excess of standard $KBrO_3$ (using methyl red) are added to the solution of the metal hydroxyquinolate in HCl; KI is then added and the iodine liberated backtitrated with thiosulfate.

$$KBrO_3 + 5KBr + 6HCl = 3Br_2 + KCl + 3H_2O.$$

$$C_9H_7ON + 2Br_2 = C_9H_5ONBr_2 + 2HBr.$$

8-hydroxyquinoline 5,7-dibromo-8-hydroxyquinoline

$$2KI + 2Br = 2KBr + 2I.$$

$$I_2 + 2Na_2S_2O_3 = Na_2S_4O_6 + 2NaI.$$

Bivalent copper, trivalent iron, interfere with the titration of 8-hydroxyquinoline by this method, as a result of the oxidation of iodide to free iodine. Poethke [2], titrated excess bromine with a solution of arsenite in the presence of p-ethoxychrysoidine, in which case copper and iron do not interfere.

Direct titration of 8-hydroxyquinoline with bromate does not give accurate results because it is difficult to determine the equivalence point with indicators.

Methods based on the oxidation of 8-hydroxyquinoline with standard permanganate [3], with quadrivalent cerium [4,5], with quinquevalent vanadium [6], and also by acidimetric methods [7], have not found wide application for a variety of reasons. Neither have methods for the direct potentiometric titration of 8-hydroxyquinoline with bromate [8,9,10], as described in the literature, which require a cathodic voltmeter or a set-up for measuring E.M.F. by compensations methods, found practical application.

The discovery of a more practical method of determining the equivalence point during direct bromatometric titration of 8-hydroxyquinoline in hydrochloric acid would lead to a simplification and a speed up in the determination of copper, iron, bismuth, manganese, and other elements by means of 8-hydroxyquinoline.

Our experiments have shown that the equivalence point can be established with reasonable accuracy by means of the simple set-up shown in Fig. 1.

The titration apparatus consists of a calomel electrode of any design with a saturated solution of potassium chloride, and a beaker containing the solution of the metal hydroxyquinolate in hydrochloric acid, in which a platinum electrode is immersed. The calomel electrode is linked to the titration solution by a ⊓ shaped tube filled with a saturated solution of potassium chloride and closed with a thick plug of filter paper. The calomel electrode is connected by a copper wire through a radio resistance of 10,000-50,000 Ω to the negative pole of a millivoltmeter or the galvanometer from a pyrometer, while the platinum electrode is connected to the positive terminal. The value of the resistance in the circuit is selected empirically so that the needle of the millivoltmeter is displaced at the equivalence point by 20-30 scale divisions on adding one drop of bromate solution. The solution of 8-hydroxyquinolate being titrated is thoroughly mixed with an electrically-driven glass stirrer.

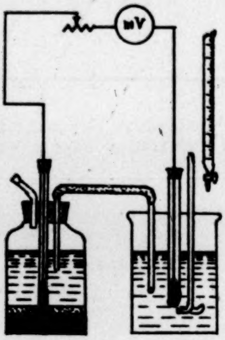

Fig. 1.

In order to study the titration of 8-hydroxyquinoline with bromate by means of the apparatus described, a standard solution of aluminum 8-hydroxyquinolate in hydrochloric acid was prepared, since the preparation of chemically pure 8-hydroxyquinoline presents some difficulty. The aluminum hydroxyquinolate was prepared by adding a 4% solution of 8-hydroxyquinoline in dilute formic acid to a weak mineral acid solution of aluminum ammonium alum containing 0.1 g Al_2O_3/100-150 ml; 30 ml of 4% hydroxyquinoline solution being used for each 0.1 g Al_2O_3. The 8-hydroxyquinoline solution was prepared as follows: 4 g of hydroxyquinoline was dissolved in the smallest possible amount of 80% formic acid, and diluted with water to 100 ml, after which ammonia was added dropwise until a faint turbidity was observed, the solution was then filtered twice through the same filter. After adding the 8-hydroxyquinoline the whole was brought to the boil and 2 N sodium acetate added dropwise. As soon as turbidity appeared no further sodium acetate was added until the precipitate became crystalline. When this occurred another 50 ml of sodium acetate solution was added for each 0.1 g of Al_2O_3 in the mixture and boiled gently for another 10 minutes. The crystalline precipitate of aluminum 8-hydroxyquinolate was filtered from the hot solution and washed, first with hot water and then cold, until the wash water was colorless. The precipitate was dried at 130° to constant weight. The exact amount of aluminum 8-hydroxyquinolate $Al(C_9H_6ON)_3$ was dissolved in HCl (1:1) in a standard flask and the solution made up to the mark with HCl (1:1).

In order to titrate 8-hydroxyquinoline, 1 g of KBr was added to an aliquot of the aluminum hydroxyquinolate solution in the titration beaker containing ca. 20% HCl, and the solution titrated with 0.1 N $KBrO_3$ with thorough agitation of the solution with the glass stirrer. The bromate was added dropwise near the equivalence point. At the equivalence point the millivoltmeter needle should move through 15-20 scale divisions when one drop is added. The needle should not return to its zero position for 2-3 minutes. If the approximate position of the equivalence point is known, titration should only take 4-5 minutes.

In order to study the effect of bivalent copper, trivalent iron, bismuth and other elements, the respective metal salt was added to the aluminum hydroxyquinolate solution contained in the titration beaker.

Typical results are adduced in the table; they show that the method is reasonably accurate and reproducible. The somewhat higher figures are probably the result of loss by volatilization of small amounts of bromine near the equivalence point when titrating in an open beaker. (Before the

Titration of 8-Hydroxyquinoline in the Presence of Various Metals

Expt. No.	Taken			Added, in g	0.1 N $KBrO_3$ used, in ml	8-Hydroxyquinoline found, in g	Error	
	Al $(C_9H_6ON)_3$, in ml	$T_{C_9H_7ON}$	8-Hydroxyquinoline, in g				Abs., g	Relative, %
1	25.0	0.003828	0.0907	–	25.3	0.0918	+0.0011	+1.2
2	25.0	0.003828	0.0907	–	25.2	0.0914	+0.0007	+0.8
3	20.0	0.002977	0.0564	–	15.55	0.0564	0	0
4	20.0	0.002977	0.0564	–	15.60	0.0566	+0.0002	+0.4
5	50.0	0.002977	0.1411	–	39.20	0.1422	+0.0011	+0.8
6	50.0	0.002977	0.1411	–	39.10	0.1419	+0.0008	+0.6
7	25.0	0.003828	0.0907	1 Bi	25.2	0.0914	+0.0007	+0.8
8	25.0	0.003828	0.0907	Ditto	25.1	0.0911	+0.0004	+0.4
9	50.0	0.002977	0.1411	0.5 Fe^{III}	39.30	0.1426	+0.0015	+1
10	50.0	0.002977	0.1411	Ditto	39.30	0.1426	+0.0015	+1
11	50.0	0.002977	0.1411	Ditto	39.30	0.1426	+0.0015	+1
12	25.0	0.003828	0.0907	0.5 Cu^{II}	25.0	0.0907	0	0
13	25.0	0.003828	0.0907	Ditto	25.1	0.0911	+0.0004	+0.4
14	25.0	0.003828	0.0907	Ditto	25.0	0.0907	0	0

equivalence point no appreciable odor of bromine is detectable, at the equivalence point a weak odor can be detected, and after the equivalence point the odor becomes quite strong). Large amounts of bivalent copper, trivalent iron, bismuth and many other metals did not appreciably affect the titration results.

Copper, iron, bismuth, magnesium, and other elements can be determined by precipitation with 8-hydroxyquinoline under suitable conditions [1]: dissolving the washed precipitates in 30-40 ml HCl (1:1), adding potassium bromide and titrating with bromate as described above. If too much metal is present the solution is diluted with HCl (1:1), made up to standard volume, and aliquots titrated.

The accuracy of the metal determinations depends on the accuracy of titration with 8-hydroxyquinoline with bromate (see Table) and the correspondence between the composition of the precipitate and its formula.

8-Hydroxyquinolate precipitates can be dissolved in technical hydrochloric acid, since trivalent iron does not interfere with the titration.

SUMMARY

A rapid and fairly accurate direct bromatometric method of titrating 8-hydroxyquinoline is described. Trivalent iron, bivalent copper, bismuth, and many other elements do not interfere.

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THE DETERMINATION OF COPPER ACETYLIDES IN THE PRESENCE OF OTHER COPPER COMPOUNDS

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It happens sometimes that it is necessary to have an accurate quantitative estimation of the amount of copper acetylides in a mixture which also contains other copper compounds (cupric oxide, basic copper carbonate, cuprous sulfide, cuprammonium compounds).

Usually the test material is treated with 10-15% hydrochloric acid for the qualitative determination of copper acetylides. The acetylene released is a proof of the presence of copper acetylides in the test mixture. This method is not suitable for quantitative determinations since the acetylene liberated is not equivalent to the copper acetylide.

The basis of the method described below is the property of potassium cyanide to decompose copper acetylides with the simultaneous evolution of acetylene in amounts equivalent to the acetylide. The reactions which occur may be expressed by the following equations

$$Cu_2C_2 + 6KCN + 2H_2O = K_4[Cu_2(CN)_6] + 2KOH + C_2H_2 \text{ - for cuprous acetylide}$$

and

$$2CuC_2 + 8KCN + 4H_2O = K_4[Cu_2(CN)_6] + 4KOH + 2C_2H_2 + (CN)_2 \text{ - for cupric acetylide.}$$

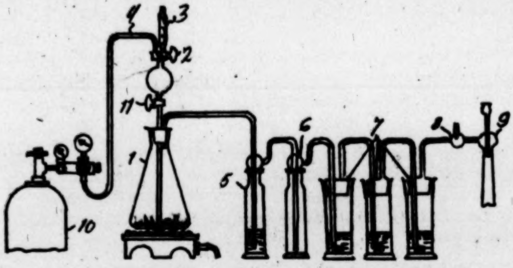
The gaseous acetylene evolved is absorbed in an ammoniacal solution of univalent copper; the copper content of the precipitated acetylide ($Cu_2C_2 \cdot H_2O$) formed is then determined iodometrically and the acetylide calculated from this.

It has been established by some workers [1,2,3] that the acetylene is quantitatively combined as the acetylide in the ammoniacal solution of univalent copper. Consequently, the amount of copper in the precipitated acetylide should correspond exactly to the amount of copper combined with the acetylene liberated by treatment of the test material with potassium cyanide solution.

Determinations were made as follows: a rubber bung with two holes was fitted into the neck of a 300 ml flask (Fig.). A special funnel was fixed in one hole; this funnel was fitted with a two way tap 2, to which was fused a small graduated funnel 3 and a branch tube 4. Through the other hole a tube was fitted which led to a series of absorbers 5,6 and 7.

Absorber 5 contains a freshly prepared suspension of ferrous hydroxide in a solution of potassium hydroxide for the absorption of cyanogen. Absorber 6 is empty and serves as a splash head. Absorbers 7, which have a capacity of 100 ml each, contain the ammoniacal solution of univalent copper (20 g cupric nitrate, 80 ml ammonia water containing 20-21% NH_3, and 60 g of hydroxylamine hydrochloride are dissolved in distilled water and the whole made up to 1 liter).

25-30 ml of solution was introduced into each of the absorbers 7. The last absorber was fitted with a three-way tap 8, whereby, if necessary the apparatus could be connected to a water pump 9. A nitrogen cylinder was connected to flask 1 via 4. An aliquot (0.1-0.2 g) of the sample was placed in flask 1, the bung replaced, and a stream of nitrogen blown through the apparatus for 2-3 minutes. When this had been done the flask was connected via the absorbent train and tap 8 to the water pump 9. As soon as a slight vacuum had been created in flask 1, 20 ml of 10% potassium cyanide was poured into funnel 3. Tap 11 was then opened wide and by carefully turning tap 2 the potassium cyanide solution was introduced into flask 1, care being taken that no air got into the flask and that the solution completely covered the sample. The flask was then connected via the two-way tap to the nitrogen cylinder, while absorber 7 was opened to the atmosphere via three-way tap 8. The nitrogen, passing through the apparatus into the absorbers, takes the acetylene with it and copper acetylides began to precipitate in the first absorber containing the univalent copper solution. The nitrogen flow was so regulated that one could count the gas bubbles. When this rate was maintained the acetylene usually did not get into the third absorber at all, and all the copper acetylide was precipitated in the first two absorbers. When no more precipitate was formed the solution in the flask was heated to the boil for 1-2 minutes in order to remove all the acetylene from solution. The copper acetylide precipitate was filtered through a filter paper, washed twice with 3% ammonia, solution and twice with water; it was then dissolved in situ on the filter paper in pure 20% hydrochloric acid, and the filter washed with distilled water, and no reaction for Cl could be detected. The hydrochloric acid filtrate was evaporated to a few mls, treated with 10 ml concentrated nitric acid, and evaporated again almost to dryness, care being taken that the residue in the flask did not darken. The practically dry residue was dissolved in 10 ml water. The solution was then treated with 25% ammonia solution until the copper complex was formed. Excess ammonia was removed by heating (till all the odor disappeared), after which 4-5 ml of 80% acetic acid was added.



Set-up for the determination of copper acetylides. 1) Flask for decomposition of the acetylides; 2) two-way tap; 3) unnel; 4) side tube; 5) absorber containing ferrous hydroxide; 6) splash head; 7) absorbers containing a solution of univalent copper; 8) three-way tap; 9) water pump; 10) nitrogen cylinder; 11) one-way tap.

The solution was allowed to stand, 10 ml of 10% KI solution added, and the solution titrated with 0.01 N sodium thiosulfate to a light straw color when starch was added, and the titration carried on to the final colorless end point.

The acetylene content calculated as Cu_2C_2 was determined by means of the formula:

$$\%Cu_2C_2 = \frac{a\cdot T\cdot 151.16\cdot 100}{2\cdot 63.57\cdot C},$$

where a is the number of mls of 0.01 N sodium thiosulfate used in the titration; T is the normality of the 0.01 N thiosulfate standardized against copper; 151.16 is the molecular weight of Cu_2C_2; 63.57 is the atomic weight of copper; C is the weight of sample, in grams.

TABLE 1

Quantitative Determination of Cuprous Acetylide

Expt. No.	Weight of metallic copper converted into cuprous acetylide, in g	Copper found in the solution after repeated decomposition of copper acetylide with hydrochloric acid, in g	Error, %
1	0.0112	0.0109	-2.8
2	0.0151	0.0152	+0.66
3	0.0151	0.0152	+0.66
4	0.0151	0.0153	+1.3
5	0.0336	0.0337	+0.3
6	0.0402	0.0394	-2.0
7	0.0402	0.0392	-2.5
8	0.0528	0.0534	+1.1
9	0.0620	0.0605	-2.4

TABLE 2

Quantitative Determination of Cupric Acetylide

Expt. No.	Weight of metallic copper converted into cupric acetylide, in g	Copper found in the solution after repeated decomposition of copper acetylide with hydrochloric acid, in g	Error, %
1	0.0174	0.0174	0.0
2	0.0250	0.0249	-0.4
3	0.0350	0.0360	+2.8
4	0.0318	0.0316	-0.6
5	0.0398	0.0384	-3.5
6	0.0400	0.0399	-0.25
7	0.0570	0.0568	-0.35
8	0.0660	0.0674	+2.1

The accuracy of the method described above was checked as follows. An accurately weighed amount of pure metallic copper was dissolved in nitric acid. This solution was neutralized with ammonia until the blue complex was formed. The complex copper solution was then decolorized by addition of hydroxylamine hydrochloride. Copper was precipitated from this reduced solution with pure gaseous acetylene. The washed precipitate of copper acetylide was introduced together with the filter into flask 1 described in the apparatus above, and decomposed with 10% potassium cyanide. The acetylene evolved was then trapped in absorbers 7 and converted again into copper acetylide, in which the copper was determined as described above. The results were calculated on the basis of copper, and not Cu_2C_2.

The suitability of this method for acetylide compounds of bivalent copper was also checked in the same way. An accurate weight of electrolytic copper was dissolved in nitric acid. After addition of ammonia to form the complex copper compound, pure acetylene was passed through the solution until it was decolorized.

The filtered and washed precipitate of the cupric acetylide was decomposed with potassium cyanide, the acetylene evolved trapped as cuprous acetylide, which was then broken down with hydrochloric acid, and the copper determined in the solution iodometrically.

The results given in Tables 1 and 2 show that the method suggested is completely suitable for the determination of copper acetylides in the presence of other copper compounds.

SUMMARY

1. It has been shown that both cuprous and cupric acetylides are decomposed by a solution of potassium cyanide to give an equivalent amount of gaseous acetylene.

2. A method is suggested for the quantitative determination of copper acetylides based on this decomposition by potassium cyanide solution, the acetylene released being trapped in a solution of univalent copper to give a pure acetylide in which copper is subsequently determined iodometrically.

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NEW COLOR REACTIONS FOR OXALATES AND SULFITES

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Reactions based on their reducing properties [1-3], are normally used for the detection of oxalates and sulfites. The majority of these methods is of low sensitivity. In order to detect small amounts of oxalates, more sensitive color reactions are used: the formation of characteristically colored compounds when oxalic acid and its salts interact with diphenylamine [4,5], with resorcinol [6], and with 2,7-dihydroxynaphthalene [7]; coupled oxidation of indigo to isatin by potassium bichromate in the presence of oxalic acid [8], etc.

The formation of characteristically colored compounds as the result of interaction between oxalates and organic materials is usually carried out in concentrated sulfuric acid and is often unreliable.

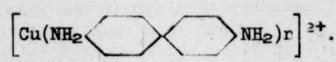
For detection of small amounts of sulfites, sensitive color reactions are employed: when sulfites react with sodium nitroprusside in the presence of potassium ferrocyanide and zinc salts, colored solutions or a colored precipitate are formed [9,10]; sulfites react with tannic materials in the presence of potassium ferricyanide to form colored compounds [11]; for the detection of sulfites in the presence of thiosulfates decolorization of fuchsin or malachite green [12], can be used; reactions based on the catalytic action of sulfur dioxide are also used, e.g. induced oxidation of nickel hydroxide (II) to nickel hydroxide (III) by atmospheric oxygen [13], the oxidation of indigo by bromates, chlorates, iodates [14,15], etc.

The formation of the difficultly soluble oxalates of calcium, thorium, and other cations is characteristic [16]. Among the reactions listed above no reactions which involve the formation of colored precipitates of oxalates or sulfites are included.

We should like to propose a new reaction for oxalates and sulfites which is based on the formation of fine, crystalline, brown precipitates when oxalates or sulfites react with an acetic acid solution of a salt of bivalent copper and benzidine.

Oxalic acid forms difficultly soluble compounds with urea [17], benzidine [18], hydrazine [19], etc. A white precipitate of benzidine oxalate is formed when oxalic acid reacts with benzidine. When oxalates react with copper salts an amorphous precipitate of copper oxalate of a pale green color is formed. It is known that sulfites react with benzidine to give a white precipitate, and with copper salts to form a lettuce-green colored precipitate which is soluble in excess sulfite.

We found that when oxalates or sulfites react simultaneously with an acetic acid solution of copper (II) and benzidine a characteristic brown precipitate is formed. Similar precipitates are formed when a ready made reagent is used which consists of a mixture of equal volumes of a 0.5% solution of benzidine in 5% acetic acid and 0.2 N cupric acetate. The reagent is a complex ion whose composition corresponds to the formula



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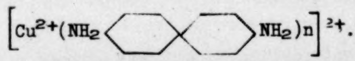
The formation of these precipitates is in full agreement with the theory of the occurrence of colored solid phased reactions advanced by Soviet scientists.

According to Kuznetsov [20] the essential condition for the occurrence of a colored solid phase reaction is the presence of a chromophore. It is, in principle immaterial whether the chromophoric groups are in the molecule of the organic reagent or whether it is the ion of the element which possesses chromophoric properties. The chromophoric action of the same element may be different for various combinations. On the other hand, the selectivity of the action of a colored solid phase reaction is related to the molecular weight and the charge of the inorganic ion. The higher the molecular weight and charge of the inorganic ion, the greater the probability that this ion can give colored solid phase reactions with a suitable organic reagent.

Yatsimirsky [21], points out that the most insoluble compounds are obtained by precipitation of large cations with large anions and vice versa.

In the reaction which we are proposing it is the copper ions which act as the chromophore; the "weighting" of the molecule is achieved by obtaining a heavy complex cation .

Analysis of the precipitate formed during reaction with oxalates showed the presence of copper ions (II), benzidine, and oxalate ions while for the reaction product with sulfite copper ions, benzidine, and sulfite were found. The presence of bivalent copper ions was established by the formation of a brown precipitate with potassium ferrocyanide and the formation of the cuprammonium complex. The presence of benzidine was established by precipitation with sodium sulfate in the form of benzidine sulfate. The presence of oxalate was checked by means of a soda extraction followed by formation of calcium oxalate in acetic acid solution and by the reaction with an acetic acid solution of bivalent copper and benzidine; sulfite ions were detected by the evolution of sulfur dioxide on treating the precipitate with acids. The precipitate containing sulfite ions was decolorized by the action of hydrogen peroxide.

Analysis of the precipitates indicated that the salts have the following probable compositions: $[Cu^{2+}(C_{12}H_8(NH_2)_2)n]C_2O_4$ and $[Cu^{2+}(C_{12}H_8(NH_2)_2)_n]SO_3$.

These reactions can probably be related to the normal type of volumetric reactions and are examples of the development of colors during interaction of organic reagents with inorganic ions, where the element itself possesses chromophoric properties, the organic reagent itself being colorless.

EXPERIMENTAL

Reactions can be carried out in a test tube, on a porcelain test plate, and on filter paper.

To 1 ml of a 0.5% solution of benzidine in 5% acetic acid solution is added 1 ml of neutral or weakly acetic acid solution of the test solution. To the white precipitate of the benzidine salt formed is added 1 ml of 0.2 N cupric acetate. In the presence of oxalate or sulfite ions the precipitate becomes brown. Heating on a water bath speeds up the reaction. To carry out the reaction on filter paper it is better to use a more concentrated solution of benzidine. 1 g of benzidine is dissolved on heating in 100 ml of 5% acetic acid. On cooling the solution, needle shaped crystals of benzidine acetate precipitate. To a drop of the solution obtained placed on a filter paper is added a drop of test solution, followed by 1 drop of 0.2 N cupric acetate. If oxalates or sulfites are present a brown spot is immediately formed.

We found that it is necessary to maintain the pH of the test solution in the range 3.5-5 in order to carry out this reaction for both oxalates and sulfites.

TABLE 1

The Effect of Benzidine Concentration on the Sensitivity of the Reaction (ratio of volume of benzidine, 0.1 N solution of cupric acetate and ammonium oxalate 1:1:1)

Conc. of benzidine in mg/ml	Effect of the reaction (Conc. $C_2O_4^{-2}$ 1 mg/ml)	Effect of the reaction (Conc. $C_2O_4^{-2}$ 0.33 mg/ml)
5	Brown precipitate	Brown turbidity, precipitate after 1 min.
3	Brown precipitate	Brown turbidity, precipitate after 1 min.
2.5	Brown precipitate after 0.5 min.	Brown turbidity, precipitate after 5 min.
2.0	Brownish-yellow precipitate after 0.5 min.	Brown turbidity, precipitate after 5 min.
1.6	Brownish-yellow precipitate after 0.5 min.	Brown turbidity, precipitate after 5 min.

The optimum concentration of benzidine is 5 mg/ml.

TABLE 2

Determination of the Reaction Sensitivity in a Test Tube (1 ml of reagents taken)

Conc. $C_2O_4^{2-}$ in mg/ml	Effect of Reaction
1	Brown precipitate
0.33	Brown turbidity, precipitate after 0.6 min.
0.25	Brown turbidity after 1 min.
0.20	Brown turbidity after 1 min.
0.15	Very weak brown turbidity after 2 min.
0.1	No precipitate

0.15 mg/ml of $C_2O_4^{2-}$ can be detected.

TABLE 3

Determination of the Reaction Sensitivity when the Reaction is Carried out on a Drop Test Plate (1 ml of each reagent taken)

Conc. $C_2O_4^{2-}$ in mg/ml	Effect of Reaction
10	Bright brown precipitate
1	Light brown precipitate
0.5	Light brown precipitate after 0.5 minute

20 μg $C_2O_4^{2-}$ can be detected in a drop of solution.

In order to determine the optimum concentrations of benzidine and the sensitivity of the reaction the series of experiments whose results are given in Tables 1,2,3 and 4 was carried out.

Table 4 shows that it is possible to determine 0.3-0.4 mg/ml of sulfite ions.

Anions which oxidize benzidine and ions which form difficultly soluble compounds with copper ions interfere. Where excess sulfate ions are present excess benzidine must be used and the reaction carried out with heating.

In order to detect $C_2O_4^{2-}$ ions in the presence of other, interfering anions, the oxalate is precipitated with calcium salts in an acetic acid medium. The precipitate is washed and then treated successively with 1-2 drops of an acetic acid solution of benzidine and cupric acetate. If oxalate ions are present the precipitate gradually acquires a brown color. Heating on a water bath favors the reaction. The reaction can also be carried out on a filter paper.

TABLE 4

Determination of Reaction Sensitivity

Conc. of $SO_3^{=}$ in mg/ml	Effect of Reaction
6.0	Brown precipitate
0.7	Brown precipitate after 0.5 min. on heating on a water bath.
0.35	Darkening of the precipitate on heating on a water bath.
0.2	No color.

A drop of test solution is placed on a filter paper and 1 drop of 1 N acetic acid and 1-2 drops of 0.5 N calcium acetate added. The paper is dried slightly, carefully washed with water and then 1 drop of benzidine (1% in 5% acetic acid) and 1 drop of 0.2 N cupric acetate placed on the spot. A brown color gradually develops if C_2O_4 ions are present.

Salts of the organic acids — acetic, tartaric, succinic, and others do not give color reactions with benzidine and cupric acetate.

SUMMARY

1. Various qualitative reactions for oxalates and sulfites have been investigated.

2. New color reactions have been found for oxalates and sulfites which are based on the formation of characteristically brown crystalline precipitates as the result of interaction between oxalates and sulfites with an acetic acid solution of copper (II) and benzidine.

3. It has been shown that the reactions proposed are sensitive and simple enough to carry out and do not require expensive reagents and apparatus.

4. The proposed reaction for oxalates has a number of advantages compared to other reactions:

a) It can be used as a spot test.

b) Oxalate ions can be detected in solid materials, e.g. in CaC_2O_4;

c) Oxalate ions can be detected in the presence of other anions and in the presence of the anions of such acids as: acetic, tartaric, succinic, etc.

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A METHOD OF CALCULATING PHOTOMETRIC CURVES DURING A STUDY OF X-RAY ABSORPTION FRINGES

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It is known the absence of a direct proportionality between the value of the blackening, and the intensity of X-rays within a wide range of change in blackening, leads to a distortion of the shape of the X-ray absorption edges registered by means of a photometer. As a consequence the absorption edges observed experimentally are usually converted with the help of blackening curves to an intensity scale, and only when this has been done are they used for calculating the curve relating absorption coefficients[1] (μ) to frequency.

The conversions mentioned above are rather difficult; a considerable amount of time is expended in carrying them out while they also presupposed a knowledge of the value of the initial intensity of the pencil of X-rays (I_0) which is not easily amenable to direct experimental determination when using the photographic method for registering spectra.

A method is advanced in this article which enables the quantitative characteristics of the absorption edges of interest to the investigator to be calculated (such as the true ratio of the intensity of individual fluctuations in the absorption coefficient in the limits of the edge and the half-width of the first line of selective absorption [2,3,4]) without resorting to the above mentioned tedious process of converting the experimental photometric curve (expressed on the blackening scale) to a curve relating absorption coefficients and frequency.

1. The basis of the proposed method is the experimentally established possibility of extending a method proposed earlier [5], which is used in optics, viz. "rectification" of the characteristic curve to the X-ray region. It has been shown experimentally[2] that the function

$$P = W + \underline{l}\,(S - W), \qquad (1)$$

where $S = \log \frac{i_0}{i}$; $W = \log\left(\frac{i_0}{i} - 1\right)$, and $\underline{l}$ is a constant.[3]

In contrast to the blackening value which is the argument of the P-transformation, P depends linearly on the logarithm of the intensity not only in the region of normal blackening but also in the region of underexposure. Experiment also showed that in all the region (from $S = 0.1$ to $S = 2$) the relation between function P and the intensity can be expressed with great accuracy by the equation

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[1] In such a case for a known range of absorbent thickness less than a certain critical value [1], curve $\mu = \mu(\underline{\nu})$ does not depend on the absorbent thickness and coincides with the curve for the absorption coefficients, which can be derived by means of ionization registration on a spectrograph with the same resolving power.

[2] Experiments were made in the wave length range 700-3000 X-units.

[3] $\underline{l}$ characteristizes the type of photographic material chosen and changes somewhat with the wave length of the radiation registered on the film.

$$P = \gamma_p \log I - i_p. \qquad (2)$$

Several methods can be advanced for finding the values of the two constants ($\underline{l}$ and γ_p) which determine the actual form of the P-transformation. The simplest of these [5], assumes a knowledge of the blackening curve. In our work we widely used for this purpose a method proposed recently [6], based on a study of the shape of X-ray emission lines.

In the absence of a blackening curve the method described below can be used. Since the ratio of the intensities of the components of the doublet $K\alpha_{1,2}$ for the elements is a constant independently of the blackening levels of these lines, a constant interval, which in practice is equal to the value of log 2, should correspond to it (the ratio) on the abscissa of the characteristic curve. At the same time because of the absence of a direct proportionality between the blackening of a line and the logarithm of its intensity, the tangent (angular coefficient) to the characteristic curve and consequently also the difference in blackening between the lines of the doublet considered ($\Delta S_{1,2}$) are different for different blackenings. On the other hand, for function $\underline{P}$ for which, according to the conditions, equation (2) should be justified in a wide blackening range, the value of $\Delta P_{1,2} = \underline{l}\Delta S_{1,2} + (1 - \underline{l})\Delta W_{1,2}$ should remain constant. The condition ($\Delta P_{1,2}$ = const.) enables one to calculate the constant $\underline{l}$ when one has measured the blackening of the $K\alpha_1$ and $K\alpha_2$ lines of the doublet, and the values of $\underline{W}$ corresponding to them in those cases where the blackening of both lines lie on a straight-line part of the characteristic curve and in the region of underexposure. At the same time on the basis of the first group of results the contrast coefficient of the film can be determined by means of the equation $\left(\gamma_s = S_{1,2}/\log 2\right)$.

A knowledge of this last coefficient in turn enables the second of the parameters characterizing the required P-transformation to be calculated. This, as shown experimentally, can be done by means of the following equation

$$\gamma_p = \gamma_s \left[\underline{l} + (1 - \underline{l}) \frac{d\bar{W}}{dS}\right], \qquad (3)$$

which is a consequence of equation (1). In the cases which we tested the value of $d\bar{W}/dS$ was equal to 1.08.

A special article [7], has been devoted to a more detailed exposition of what has been described above, and of certain other methods of finding the parameters of the P-transformation, as well as of experiments using the latter for carrying out X-ray spectrographic analysis.

2. By using the P-transformation described above it is possible to simplify and speed up the method of calculating experimental photometric curves of X-ray absorption edges considerably. It is not difficult to show that in the case considered, a change from the scale of blackening $\underline{S}$ in which the experimental absorption edges are usually represented, to the P-scale is physically equivalent to a direct conversion of the experimental curve to a curve of absorption coefficients. In fact during investigations of the fine structure of X-ray absorption edges photometrically, the value of the intensity I, acting on a film in the limits of the edge, is related to the absorption coefficient of the absorbent by the relation

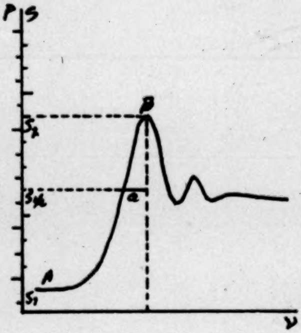
$$I = I_0 e^{-\mu d}.$$

Consequently

$$P = P_0 - 0.43\gamma_p \mu d, \qquad (4)$$

throughout all the blackening interval for which the use of equation (2) is justified. Here $P_0 = \gamma_p \log I_0 - i_p$.

By means of equation (4) it is possible to determine directly the true relation between the intensity of fluctuations of the absorption coefficient and the half-width of the first line of selective absorption on the basis of a few measurements of the original experimental curve expressed on a blackening scale.



Let us consider, e.g., the typical experimental absorption edge represented on the diagram. Let the blackening of the points A and B be S_1 and S_2 and the values of the absorption coefficients corresponding to them μ_1 and μ_2. From formula (4), it follows that the ratio of absorption coefficients in which the investigator is interested, at any point on the edge characterized by the numbers S_x and μ_x, to the first absorption maximum can be obtained from the relation

$$\frac{\mu_x - \mu_1}{\mu_2 - \mu_1} = \frac{P_1 - P_x}{P_1 - P_2}, \qquad (5)$$

in which the values of P_1, P_2 and P_x are calculated from formula (1) according to the known blackening values.

Similarly, it is also possible to determine the half width of the first line of selective absorption directly from the experimental curve (see diagram); it is equal to the width of the absorption line measured at a blackening value ($S_{1/2}$) which corresponds to the value $P_{1/2} = \frac{P_1 + P_2}{2}$ 1).

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1) This follows directly from equation (5) under such conditions that $\frac{\mu_x - \mu_1}{\mu_2 - \mu_1} = \frac{1}{2}$. In the general case for the relation $\frac{\mu_x - \mu_1}{\mu_2 - \mu_1} = \frac{1}{n}$, $P_n = \frac{P_1 + (n-1)P_2}{n}$

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THE NATURE OF THE SO-CALLED "WEIGHTING EFFECT"

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In 1924 Feigl [1], postulated that an increase in the molecular weight of a reagent which is capable of forming a precipitate, as a rule, increases the sensitivity of the reaction. A similar type of effect has received the name "weighting effect". Feigl relates the solubility of the compound formed to its molecular weight [2].

It has been established however, in the work of Kuznetsov [3,4], and Kulberg [5], that solubility does not always decrease with increasing molecular weight, and that when the "weighting effect" is used the functional-analytical groups should not be touched.

In Kulberg, Mustafin, and Kochetkov's latest paper [6], it has been shown that it is also essential to take the chemical nature of the "weighting" group into consideration and the position of this group in the reagent molecule.

Despite a considerable amount of work which has been devoted to the "weighting effect", the nature of this effect still remains unexplained and even the term itself does not reflect the true nature of things, since there is no relation between solubility and molecular weight of a compound. High molecular weight compounds are known which have good solubilities, while low molecular weight compounds are known with low solubilities. Solubility may be reduced not only by increasing the molecular weight, but also by decreasing it (e.g. the substitution of sulfo or hydroxyl groups by hydrogen). A large number of groups are known which can increase the molecular weight and the solubility of a substance.

We can imagine that the solution process of an organic material takes place in two stages as we did in the case of the solubility of inorganic materials [7,8].

1. Break up of a given substance into separate gaseous molecules (ions) which do not interact. This process is connected with a free energy change which we shall denote by W. W in a given case is the free energy of the crystal lattice [7].

2. A transfer of the gaseous molecules (ions) of the given substance into solution. The free energy change occurring during this stage we shall denote by F. Here F is the free energy of solvation of the molecules or the total free energy of ionic solvation. In the case of aqueous solutions, F is the free energy of hydration.

The change in free energy during the process

$$AB_{solid} + Solv. = AB_{Solv.} \qquad (I)$$

can be expressed by the following relation:

$$nRT \ln a = F - W, \qquad (1)$$

where n is the number of ions into which the electrolyte molecule breaks up (for non-electrolytes n = 1) and a is the activity of a saturated solution of the given substance. For simplification the solubility S may be used as an approximation to the activity, under standard conditions therefore we get:

$$1.36n \log S = F - W. \qquad (2)$$

The introduction of a group R into compound AB leads to a change in the free energy of solvation (ΔF) and in the free energy of the lattice (ΔW), and consequently to a change in the solubility ($\Delta \log S$).

The introduction of a non-polar group or a group of low polarity leads to a decrease in the free energy of solvation, since the introduction of this group into a solvent leads to a disruption of its structure and to the formation of new surfaces of separation R...Solv. (in the special case R...H_2O).

A decrease in the absolute value of the free energy of solvation can be calculated by means of the formula:

$$-\Delta F = N\sigma\Delta S, \qquad (4)$$

where ΔS is the increase in area of a molecule on introducing group R; σ is the free energy of unit surface of R...Solv., and N is the Avogadro number.

Equation (4) opens up a way of calculating quantitatively the effect of various groups on the solubility of organic compounds. Thus using Hartley's [9], and Meggy's results [10], for the surface C-H...H_2O we get:

$$-\Delta F = 0.043\Delta S \qquad (4a)$$

In this equation ΔS is expressed in square Angstroms, and ΔF in kilocalories. Relation (4a) would be justified under such conditions that on introducing the molecule of the organic material into solution there would be no interaction between the individual water molecules.

In actual fact the molecules of water are not separated by an infinite distance and interaction occurs between them which amounts to, according to Meggy [10], approximately half the total free energy.

Consequently, on introducing a hydrocarbon radical into aqueous solution the decrease in free energy amounts to:

$$-\Delta F = 0.021\ \Delta S. \qquad (5)$$

As an example let us calculate $-\Delta F$ for the CH_2 group. In the literature [10], CH_2 is regarded as a rod of length 1.27 A and with a cross-sectional area of 18.5 A^2. From which, for CH_2 ΔS amounts to 19.3 A^2 and $-\Delta F = 0.415$ kcal/mol.

Similar calculations can be made for other hydrocarbon radicals (C_6H_5–, $C_{10}H_7$– etc.).

In all these cases, a lyophobic group R is introduced into the molecule AB and the solubility of the compounds formed decreases.

Cases are also possible where the groups introduced can react with the solvent, forming hydrogen or dipolar bonds (e.g., the groups OH, COOH, SO_3H and others with water). In such cases the free energy of solvation increases in absolute water ($\Delta F > 0$) while the solubility of the compound formed also increases.

Finally, cases are possible where introduction of a group R into molecule AB does not essentially affect the free energy of solvation. The halogens (Cl, Br, I) belong to this category. In connection with the fact that the covalent radii of the halogen atoms are considerably greater than the covalent radius of the hydrogen atom, substitution of hydrogen by halogen leads to an increase in the surface of the molecule (ion), and as a consequence of the lyophobic effect considered above, lowers the free energy of hydration. In such cases, however, polarity is manifested in the molecule (ion) as well as the possibility of dipolar interaction between the molecules of dissolved material and solvent molecules, as a result of which the free energy of hydration increases. The presence of these two opposing factors should lead in the final count to an insignificant change in the free energy of hydration when hydrogen is substituted by a halogen.

It can be postulated that any group R introduced into a reagent molecule leads to a definite (always roughly constant) change in the value of the free energy of solvation (ΔF). This change is determined by the nature of the group and can vary both in sign and in magnitude for different groups.

The change in free energy of solvation depends not only on the nature of the group R, but also on the nature of the solvent. Thus, the introduction of hydrocarbon radicals which are hydrophobic decreases the solubility of various compounds in water, but does not essentially affect the solubility of the same compounds in solvents of the benzene type, in relation to which the hydrocarbon radicals are not lyophobic. This fact once again indicates the unhappy choice of the term, "weighting effect" – "weighting" leads to a decrease in solubility in certain solvents and does not affect the solubility of a given group of compounds in other solvents.

Introduction of a group R into the molecule of a given material not only affects the free energy of solvation, but essentially affects the free energy of the molecular lattice. We have considered the concept of the free energy of ionic compounds previously [7]. The free energy of a lattice for compounds with a molecular lattice can be expressed by the simple relation:

$$W = -RT \ln p, \qquad (6)$$

where p is the vapor pressure of a given compound.

Increasing the molecular weight of organic compounds as a rule actually leads to a decrease in vapor pressure and consequently to an increase in the free energy of a molecular lattice. From equations (1) and (3) it follows that an increase in W should decrease the solubility, and from this point of view the term "weighting effect" should have some justification. In a large number of cases, however, the increase in W is compensated by a significantly large increase in the free energy of solvation F. Moreover, in a whole series of cases an increase in molecular weight leads, not to an increase in the free energy of the lattice (to a decrease of vapor pressure), but to a decrease. Thus, the substitution of hydroxyl by any halogen is accompanied by an increase in molecular weight, together with which the vapor pressure of the halogen derivatives is greater than that of the corresponding alcohols. The vapor pressure of the halides decreases steeply in the order RF, RCl, RBr, and RI.

When a CH_2 group is introduced, the free energy of the lattice increases on an average by the same amount. Results for liquids are given in Table 1; from this table it is evident that the difference in RT ln p in this case amounts to 0.46 kcal on an average.

If we assume that this regularity is maintained for solid compounds as well, then the decrease in solubility ($\Delta \log S$) on introducing a CH_2 group should be −0.63 in accordance with equations (3) and (5).

The results given in Table 2 confirm this assumption; on going from one member to another of a homologous series, the logarithm of the solubility decreases by an average of 0.60.

TABLE 1

Change in the vapor pressure of an homologous series (vapor pressure in mm of mercury at 20°C)

Compound	log p	$-\Delta$log p	Compound	log p	$-\Delta$log p
CH_3COOH	1.07				
C_2H_5COOH	0.76	0.31	CH_3OH	1.98	
C_3H_7COOH	0.45	0.31	C_2H_5OH	1.65	0.33
C_6H_5	1.87		C_3H_7OH	1.18	0.47
$C_6H_5CH_3$	1.45	0.42	C_4H_9OH	0.70	0.48
$C_6H_5C_2H_5$	1.18	0.27	$C_5H_{11}OH$	0.44	0.26
$C_6H_5C_3H_7$	1.00	0.18			
Mean	-	0.30	Mean	-	0.38

It is conceivable that the introduction of other groups will decrease (or increase) the free energy of a molecular lattice by approximately the same amount, and that for each group there is its own specific increment Δ log S.

An exact calculation of the free energy change of a molecular lattice as the result of introducing various groups into a molecule is impossible at present. Calculation is complicated by the fact that in a given case the mutual effect of atoms and the position of the group introduced is particularly strong. Nevertheless, as a very crude approximation one might in the first place assume that the introduction of the same group into different molecules leads to the same change in free energy of the lattice, and consequently of Δ log S.

TABLE 2

Solubility of organic compounds in water

Compounds	$-$ log S	$-\frac{\Delta \log S}{n^{1)}}$	Compounds	$-$ log S	$-\frac{\Delta \log S}{n^{1)}}$
Hydrocarbons			Carboxylic acids		
C_5H_{12}	2.30		C_4H_9COOH	0.48	
C_6H_{14}	2.80	0.50	$C_5H_{11}COOH$	1.03	0.55
C_7H_{16}	3.28	0.48	$C_6H_{13}COOH$	1.77	0.74
C_8H_{18}	3.88	0.60			
$C_6H_5CH_3$	2.29		Complex esters		
$C_6H_5C_3H_7$	3.30	0.51	CH_3COOCH_3	-0.63	
			$CH_3COOC_2H_5$	0.01	0.64
Alkyl Halides			$CH_3COOC_3H_7$	0.73	0.72
C_3H_7Cl	1.46		$CH_3COOC_4H_9$	1.36	0.63
C_4H_9Cl	2.15	0.69	$CH_3COOC_5H_{11}$	1.86	0.50
C_2H_5Br	1.08		$C_2H_5COOCH_3$	0.13	
C_3H_7Br	1.70	0.62	$C_2H_5COOC_2H_5$	0.63	0.50
CH_3I	1.05		$C_2H_5COOC_3H_7$	1.37	0.74
C_3H_7I	2.25	0.60	$C_3H_7COOCH_3$	0.82	
C_4H_9I	2.96	0.71	$C_3H_7COOC_2H_5$	1.23	0.51
			$C_3H_7COOC_3H_7$	1.89	0.66
Alcohols			$CH_3COOC_2H_5$	0.01	
$C_6H_{13}OH$	1.24		$C_2H_5COOC_2H_5$	0.63	0.62
$C_7H_{15}OH$	1.81	0.57	$C_3H_7COOC_2H_5$	1.23	0.60
			$C_4H_9COOC_2H_5$	1.74	0.51
			$C_7H_{15}COOC_2H_5$	3.44	0.57

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1) n=number of CH_2 groups

The results given in Table 3 confirm this assumption. The exception is the carboxyl group; its introduction instead of hydrogen into the aliphatic and aromatic compounds leads to a different effect.

TABLE 3

Solubility of organic compounds in water

Compounds	R=H	R=Cl		R=Br		R=I		R=OH		R=COOH	
	$-\log S$	$-\log S$	$\Delta\log S$	$-\log S$	$\Delta\log S$	$-\log S$	$\Delta\log S$	$-\log S$	$\Delta\log S$	$-\log S$	$\Delta\log S$
C_3H_7R	(1.20)	1.46	-0.26	1.70	-0.50	2.25	-1.05				
C_4H_9R	(1.70)	2.15	-0.45			2.96	-1.26			0.48	1.32
$C_5H_{11}R$	2.30									1.03	1.27
$C_6H_{13}R$	2.80							1.24	1.56	1.77	1.03
$C_7H_{15}R$	3.28							1.81	1.47		
C_6H_5R	1.98	2.36	-0.38	2.55	-0.57	2.78	-0.80	0.15	1.83	1.66	0.32
$C_{10}H_7R$	3.63							2.29	1.34	3.40	0.23
Mean $\Delta\log S$			-0.36		-0.53		-1.04		1.55		-

Substitution of hydrogen in the C-H group by various other groups leads to a change in solubility, which can be characterized by an increment ($\Delta\log S$) which is approximately constant for each group. (Increment $\Delta\log S$ is a difference between the logarithm of the solubility of two comparable compounds). In the case of the hydroxyl group $\Delta\log S$ has a mean value of 1.5 (an increase in solubility of approximately 30 times); for the other atoms and groups considered here $\Delta\log S$ is negative and has the following approximate values: CH_3 -0.60; C_6H_5 -2.1; Cl -0.4; Br -0.5; I -1.0. Variation in the value of $\Delta\log S$ can be explained by the mutual effects of various groups on the molecule of the substances considered.

In conclusion we shall consider the effect of various groups on the solubility of salts and salt forming compounds. This effect is of particular interest to the analyst, since such compounds are obtained during the majority of reactions. In those cases, where the reacting centers are not touched, when a new group is introduced the free energy of the lattice of the salt or salt forming compound does not change, or changes by very little ($\Delta W \approx 0$), and the change in solubility is determined by the change in the free energy of solvation of the salt ions:

$$1.36n \ \Delta\log c = \Sigma\Delta Fi. \qquad (7)$$

Actually, the distances between the metal ions and the active groups of reagent ions remain unchanged, if the 'weighting' groups are introduced in the farthest parts of the reagent. We demonstrated [11], that the thermochemical radii of the $HCOO^-$, CH_3COO^- and $C_2H_5COO^-$ ions remain constant despite a change in the absolute dimensions of these particles.

The solubility of the lithium, calcium, and barium salts of various carboxylic acids is compared in Table 4. These results show that on the introduction of each new CH_2 group the logarithm of the solubility decreases by an average of 0.25. This decrease corresponds to a decrease in the free energy of solvation of the acid anion of 0.34 kcal; using equation (5) we got a value of 0.41 kcal.

The introduction of new aromatic rings leads to an even greater decrease in solubility.

In conclusion we shall consider a few examples which illustrate the application of the hypothesis advanced above in analytical chemistry.

There is a definite relation between the sensitivity of a reaction and the solubilities of the reaction products. Although a number of other factors (color of the precipitate, its character, the rate at which it is formed, etc.) also affect the sensitivity [2], nevertheless, the effect of solubility on sensitivity remains the decisive one.

TABLE 4

Solubility of carboxylates

Salts	$-\log S$	$-\dfrac{\Delta \log S^{1)}}{n^{2)}}$	Salts	$-\log S$	$-\dfrac{\Delta \log S^{1)}}{n^{2)}}$
$C_{11}H_{23}CO_2Li$	2.08				
$C_{15}H_{31}CO_2Li$	3.16	0.27	$(C_6H_{13}CO_2)_2Ba$	1.40	
$C_{17}H_{35}CO_2Li$	3.62	0.24	$(C_7H_{15}CO_2)_2Ba$	1.83	0.22
$(C_3H_7CO_2)_2Ca$	0.07		$(C_8H_{17}CO_2)_2Ba$	2.51	0.34
$(C_5H_{11}CO_2)_2Ca$	1.09	0.25	$(C_{11}H_{23}CO_2)_2Ba$	4.00	0.25
$(C_7H_{15}CO_2)_2Ca$	2.02	0.23			
$(C_8H_{17}CO_2)_2Ca$	2.40	0.19			

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1) Mean value $\Delta \log S = 0.25$.

2) n = the number of CH_2 groups.

In the majority of cases, salt-like substances are precipitated, the rules for the solubility of which have been considered above. Substitution of the hydrogen in a CH group by a methyl group leads to a decrease in the logarithm of the solubility of 0.25, i.e., the solubility is halved. One would expect therefore that the limit of identification would in such a case also be doubled. In addition to the numerous examples considered above, we may point out that on switching from HC(NOH)CHNOH to methylglyoxime, the sensitivity of the reaction for nickel is doubled.

The introduction of new aromatic rings into a reagent leads to an even greater decrease in solubility. In the case of salt-like reaction products the logarithm of the solubility decreases by 0.7-1.3 (the solubility decreases by 5-20 times). The sensitivity changes by roughly the same amount. This regularity can be observed on comparing the sensitivity of the reactions for bismuth in which various organic bases are used (α-picoline, quinaldine, β-naphthoquinaldine, etc.).

Examples given by L. M. Kulberg [5] show that the introduction of a sulfo group into a reagent leads to an increase in solubility of 5-10 times.

The introduction into a reagent molecule of lyophobic groups leads to a decrease in solubility not only of the reaction product, but also of the reagent itself. The latter in the long run may mean a decrease in the sensitivity. In all cases, therefore, there is a definite limit to an increase in reaction sensitivity which is related to the fact that the solubility of the reagents decreases more rapidly than that of the reaction products, which in the majority of cases are salt-like compounds.

SUMMARY

The introduction of various groups into an analytical reagent leads to a change in the free energy of solvation of the reaction product formed which is of low solubility, and in the free energy of the lattice. In the simplest cases the change in free energy of hydration can be calculated.

On substitution of the hydrogen in a C–H group by a particular group there is a constant change in the logarithm of the solubility. The effect of each group on the solubility of the compounds formed (and consequently on the sensitivity of an analytical reaction) can be characterized semi-quantitatively. In assessing the phenomena considered quantitatively it is necessary to bear the mutual effects of the respective groups in mind.

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OSCILLOGRAPHIC POLAROGRAPHY

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In the last few years a number of articles has appeared [1] which have been devoted to the study of reduction processes of certain ions on the dropping mercury cathode by means of oscillographic polarography.

While in ordinary polarography the e.m.f. is applied to the electrolyzer fairly slowly, at the rate of about 0.005 V per second, so that one is unable to study rapid processes, it is possible, by the use of oscillographic polarography, to attain a very rapid rate of voltage application to the cell of up to 10^2 V per second and higher.

This enables many chemical processes occurring on the dropping mercury electrode to be studied from different aspects.

We constructed an oscillographic polarograph, the general appearance of which is illustrated in Fig. 1 (see plate, page 363), where I is the oscillographic polarograph; II is the electronic oscillograph; III is a vacuum tube voltmeter; IV is a voltmeter or potentiometer; and V is the electrolytic cell, consisting of a dropping mercury cathode and a saturated calomel electrode (the electrolytic cell is screened in order to prevent interference with the oscillographic curve.

The set-up used is shown schematically in Fig. 2.

1. Description of the Oscillographic Polarograph. A saw-tooth wave voltage generator feeds the horizontal deflecting plates 1 and 2 of the oscillograph. This saw-tooth voltage with a given voltage amplitude regulated by a voltage amplifier is applied to the electrolyzer electrodes, which are connected in series with a resistance box. As a result of the application of a definite voltage to the polarographic cell containing the test solution, a current develops. After amplification, this current is applied to the vertical deflecting plates 3 and 4. With this set-up, the horizontal deflection is proportional to the voltage applied

to the polarographic cell, while the vertical deflection is proportional to the current flowing through the polarographic cell.

It is known that by changing the value of the voltage applied to the cell containing the test solution, it is possible to observe the beginning of the reduction or oxidation of an ion on the dropping mercury cathode by the sharp change in the value of the current passing through the cell.

Knowing the value of the voltage at which reduction or oxidation of an ion starts on the dropping mercury cathode, it is possible to detect a particular chemical element in solution.

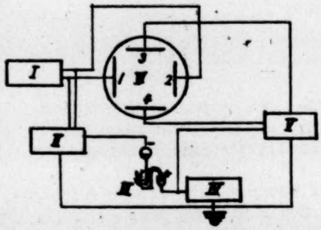

Fig. 2. Schematic diagram of the oscillographic polarograph:
- I – Saw-tooth wave voltage generator;
- II – voltage amplifier;
- III – cell;
- IV – resistance box;
- V – current amplifier;
- VI – oscillograph

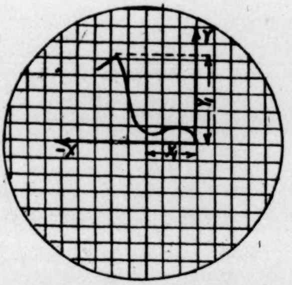

Fig. 3. An oscillographic curve for lead.

A further increase in the voltage applied to the electrolytic cell after attaining the reduction or oxidation potential for a particular ion leads to an increase in the current passing through the electrolytic cell to a certain maximum value. From this maximal peak current passing through the cell, it is possible to determine the concentration of the test ion in solution.

The oscillographic polarograph which we built gave oscillograms (Fig. 3) where the voltage applied to the cell lies along the abscissa, while the values of the current passing through the polarograph cell lie along the ordinate. Coordinates (x_1, y_1) characterize a particular element and its concentration in solution.

For determination of the concentration of a test ion, only the largest curve which depicts the reduction or oxidation of the ion on one drop of mercury with a maximum area (this corresponds to the point of detachment of the drop from the capillary) is taken into consideration.

In constructing this oscillographic polarograph several modifications were made of the set-up proposed by Delahay [2].

The radio-technical set-up consists of several stages with different functions: 1) a saw-tooth wave voltage generator; 2) an amplifier for the saw-tooth wave voltage applied to the electrolyzer; 3) an amplifier for the current passing through the polarographic cell; 4) a supply source (for anode voltage and filament heating).

Essential modifications were made to the saw-tooth voltage amplifier and the current amplifier, respectively, in order to increase the sensitivity.

The Saw-tooth Voltage Generator. The generator supplies a saw-tooth voltage (Fig. 4) with an amplitude up to 200 V. The frequency of the oscillations generated can be changed from 1 to 50 cycles. With such a frequency it is possible to change the time taken for the voltage to grow to its maximum from 1 to 1/50 second. A time of 1/50 second between two successive voltage peaks overlaps the time necessary for the ion reduced on a drop to be oxidized again.

The most suitable operating frequency in the case of saw-tooth voltages is from 5 to 20 sweeps/second.

The saw-tooth voltage depicted in Fig. 4 is applied directly from the generator to the horizontal deflecting plates. The frequency of the saw-tooth oscillations of the generator can be measured if it is applied to the horizontal deflecting plates, while at the same time an alternating voltage with a period of 50 cycles is applied to the vertical deflecting plates from the circuit. The generator frequency will then be $n = 50/n$,[1] where n is the number of sweeps observed on the oscillograph screen.

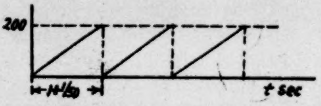

Fig. 4. Saw-tooth voltage with an amplitude of up to 200 V.

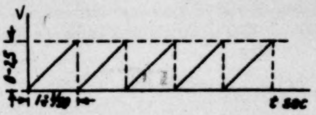

Fig. 5. Amplitude value of the saw-tooth voltage from 0 to 2.5 V.

Voltage Amplifier. The saw-tooth voltage amplifier is capable of applying a saw-tooth voltage with an amplitude of 0 to 2.5 V to the cell (Fig. 5).

For any chemical element in the test solution, therefore, it is possible to select a particular voltage for applying to the cell such that the element is reduced on the dropping mercury cathode.

The magnitude of the saw-tooth voltage can be measured with a vacuum tube voltmeter or potentiometrically (the voltmeter or potentiometer is connected to the electrodes of the polarographic cell):

$$V_{\sim} = 2(V_{\text{meas.}} - V_{=}), \qquad (1)$$

---

[1] In subsequent experiments we used a mechanical counter which registered the number of sweeps/unit time for determining the frequency of the saw-tooth generator vibrations.

where $V_{\sim}$ is the value of the saw-tooth voltage applied to the cell; $V_{=}$ the value of the negative constant voltage applied to the cell and $V_{meas.}$ the value measured potentiometrically or by means of a vacuum tube voltmeter.

In order to avoid distortions introduced by interference, measurements were made before registering the oscillogram.

Current Amplifier. The current amplifier is designed for increasing the weak currents developed in the cell to a value which can be registered by the oscillogram.

Its operating conditions are sensitive to electromagnetic interference and to the micro-background effect (particularly for low concentrations and currents). These are removed by screening and damping the current amplifier.

Supply Source. A suitable source of anode supply for this particular set-up is one provided by an electronic voltage stabilizer for 60-80 mA. Filament heating is supplied by an accumulator.

In order to avoid distortion the anode supply source is placed at some distance from the polarographic cell.

II. A Consideration of the Oscillograms Obtained During the Reduction of Certain Ions on the Dropping Mercury Cathode.

As examples of the sort of polarograms obtained we adduce Figs. 6 and 7 for solutions of 10^{-4} M $CdCl_2$ and 10^{-4} M $ZnCl_2$ in N KCl.

Electrolysis was carried out using a saw-tooth voltage of amplitude 1.8 V in the presence of dissolved atmospheric oxygen. Fig. 6 shows a number of oscillographic curves obtained for one drop of mercury during its growth, while Fig.7 shows the maximal curve for one mercury drop.

The first maximum on the right corresponds to the maximum capacity current. The second maximum is the result of the reduction of cadmium ions, while the third and fourth maxima correspond to zinc reduction on the dropping mercury cathode. The fourth maximum is small compared with the third. This is clearly shown in Fig. 7.

The oscillographic waves of cadmium and zinc whose appearance at -1.12 and -0.60 V relative to the saturated calomel electrode are clearly defined and can be measured accurately. The fourth maximum on the curve is caused by dissolved atmospheric oxygen.

In order to determine the effect of dissolved atmospheric oxygen on the reduction of cadmium and zinc ions (on the dropping mercury electrode) we electolyzed the same solutions after removal of dissolved oxygen, using the same value for the amplitude of the saw-tooth voltage as before.

Fig. 8 shows what happens during the life of a drop. We can clearly see the oscillographic waves for cadmium and zinc. When the curves on Figs. 6 and 8 are compared, it is not difficult to see that oxygen affects the zinc reduction to a greater extent than the cadmium reduction. In test solutions free from dissolved oxygen the second zinc maximum disappears.

Fig. 9 shows a polarogram for one maximal curve of the mercury drop, where we can distinctly see waves for cadmium and zinc which appear on the curve at potentials equal to those which are characteristic of cadmium and zinc in normal polarography.

The oscillograms in Figs. 10 and 11 are for 0.1 N potassium chloride containing $2 \cdot 10^{-5}$ M $CdCl_2$ and $1.9 \cdot 10^{-5}$ M $ZnCl_2$. Electrolysis was carried out in the presence of dissolved atmospheric oxygen at the same saw-tooth voltage amplitude used before.

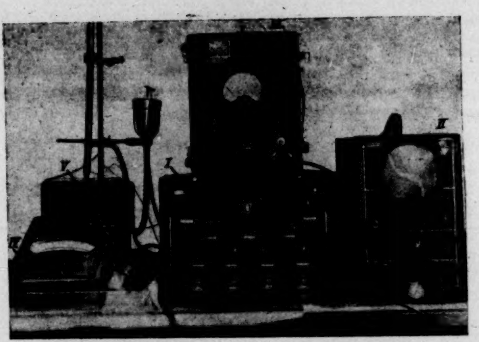

Fig. 1. General appearance of the oscillographic polarograph.

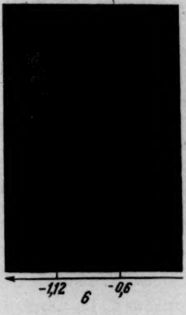

Fig. 6. Oscillographic curves for Cd^{2+} and Zn^{2+} for one drop during its growth; m = 2.6 mg/sec, t = 3.5 sec, v = 18 V/sec.

Fig. 7. Oscillographic curve for Cd^{2+} and Zn^{2+} for a maximal cross-sectional area of the mercury; m = 2.6 mg/sec, t = 3.5 sec, v = 18V/sec.

Fig. 8. Oscillographic curves for cadmium and zinc on 1 drop of mercury during its growth; m = 2.6 mg/sec, t = 3.6 sec, v = 18V/sec.

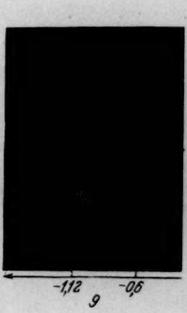

Fig. 9. Oscillographic curves for cadmium and zinc on 1 drop of mercury at its maximal cross-sectional area; m = 2.6 mg/sec, t = 3.5 sec, v = 18 V/sec.

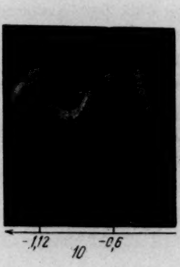

Fig. 10. Oscillographic curves for cadmium and zinc on 1 drop of mercury during its growth; m = 2.6 mg/sec, t = 3.5 sec, v = 18 V/sec.

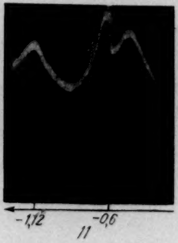

Fig. 11. Oscillographic curve for cadmium and zinc on 1 drop of mercury at its maximal cross-sectional area, m = 2.6 mg/ t = 3.5 sec, v = 18 V/sec

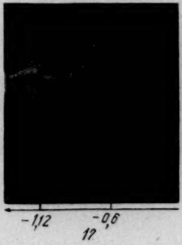

Fig. 12. Oscillographic curves for cadmium and zinc on 1 drop of mercury during its growth; m = 2.6 mg/sec, t = 3.5 sec, v = 18V/sec.

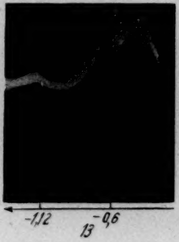

Fig. 13. Oscillographic curves for cadmium and zinc for 1 drop of mercury at its maximal cross-sectional area; m = 2.6 mg/sec., t = 3.5 sec, v = 18 V/sec.

Fig. 10 shows what happens during the life of a drop. Though the concentration of the test ions in solution was five times less than in the previous experiments, the cadmium and zinc waves are still well defined.

Fig. 11 is a maximal curve. After removal of oxygen from the 0.1 N KCl containing $2 \cdot 10^{-5}$ M $CdCl_2$ and $1.9 \cdot 10^{-5}$ M $ZnCl_2$, the values for the maximal zinc and cadmium currents are less than the corresponding maximal values in solutions containing atmospheric oxygen (See Figs. 12 and 13).

Figs. 12 and 13 show that dissolved oxygen has a greater effect on the reduction of zinc than on the reduction of cadmium (compare Figs. 11 and 13). In the absence of oxygen, the strict linear relation between the test ion concentration and the value of its maximal current is still maintained when the rate of change of potential remains constant during the experiment. Since the rate of change of the saw-tooth voltage applied to the electrolytic cell has an appreciable effect on the height of the maximal curve of the test ions we carried out a number of experiments in order to study this effect.

Effect of the Rate of Potential Change on the Value of the Maximal Current of the Reduced Ion.

The rate of change of the applied potential depends on the frequency of the generator (ν) and on the amplitude of the saw-tooth voltage ($V\sim$). The product of these two quantities gives the rate of change of the saw-tooth potential applied to the electrolytic cell.

10^{-4} M $CdCl_2$ in 0.1 N KCl and 10^{-4} M $ZnCl_2$ in 0.1 KCl, respectively, were tested in the absence of atmospheric oxygen at various rates of potential change. Electrolysis was carried out using two dropping mercury electrodes with different drop times. Randles [3], derived an equation for the maximal value of the ocsillographic wave when a dropping mercury cathode is used; it is of the following form:

$$I_{max} = \frac{1.24\pi F}{(0.0118)^{1/2} 10^3} n^{3/2} \gamma^{2/3} t^{2/3} \underline{v}^{1/2} D^{1/2} c, \qquad (2)$$

where I_{max} is the maximal current of the oscillographic wave expressed in amperes; F - the Faraday number; n - the number of electrons participating in the reaction; γ is related to the expression $r_0^3 = \frac{3mt}{4\pi d} = \gamma t$, i.e., $\gamma = \frac{3m}{4\pi d}$ (where m is the amount of mercury in grams issuing from the capillary in 1 second; d - the density of mercury; t - the drop time); v - the rate of change of potential in volts per second; D - the diffusion coefficient of the reduced ion; and c - the ionic concentration expressed in mols per liter.

We calculated the maximal current by means of equation (2) and compared the results with the experimental results. They are adduced in Table 1.

The table shows that the experimental results do not agree with the calculated ones. For reductions of Cd^{2+} on a dropping mercury cathode, the deviation between calculated and experimental values is as much as 21%, and this deviation increases with increasing rate of potential change.

Since the zinc ion is reduced irreversibly on the dropping mercury cathode, the percentage deviation between experimental and calculated is considerably greater.

This deviation of the experimental values from those calculated by means of Randles' equation is a consequence of the fact that Randles derived his equation for the maximal current on the basis of a differential equation for linear diffusion, instead of an equation for convective diffusion to the surface of the expanding drop.

TABLE 1

The Effect of the Rate of Potential Change on the Value of the Maximal Current of the Reduced Ion

Amplitude of the saw-tooth voltage, in volts. ($V_{\sim}$)	Frequency of the saw-tooth voltage generator (ν)	Rate of change of voltage, in volts (v)	Maximal current of the reduced ion		Difference in % between calculated and experimental values [1]
			Found μA	Calculated from (2) μA	
10^{-4} M $CdCl_2$ in 0.1 N KCl; $D_{Cd^{2+}} = 0.52 \cdot 10$ cm^2/sec; m = 2.18 mg/sec; t = 3.5 sec; h = 280 mm					
-1.22	1.25	1.53	5.81	7.25	~19.9
-1.22	2.27	2.77	7.80	9.75	~20.0
-1.22	6.25	7.63	12.7	16.18	~21.5
-1.22	7.16	8.74	13.7	17.32	~21.0
10^{-4} M $CdCl_2$ in 0.1 N KCl; m = 0.76 mg/sec; t = 8.28 sec; h = 470 mm					
-1.1	3.0	3.3	7.50	9.35	~19.8
-1.00	6.2	6.2	10.0	12.83	~22.0
-1.00	8.3	8.3	11.24	14.84	~24.2
-0.86	10.0	8.6	11.8	15.11	~21.8
-0.98	16.6	~16.3	16.2	20.81	~22.0
10^{-4} M $ZnCl_2$ in 0.1 N KCl; $D_{Zn^{2+}} = 0.5 \cdot 10^{-5}$ cm^2/sec; m = 0.76 mg/sec; t = 6.4 sec; h = 470 mm					
-1.66	3.57	5.93	6.54	10.36	36.9
-1.58	7.10	~11.22	8.66	14.24	39.2
-1.62	10.00	16.2	10.30	17.13	39.8
-1.44	12.50	18.0	10.71	18.06	40.7
-1.66	16.60	27.56	11.8	22.34	47.2

[1] The calculated values are taken as 100%.

Moreover, in deriving his equation Randles postulated that the concentration of the test ion in solution is equal to the concentration of the same ion near the surface of the mercury drop plus the product of the metal concentration in the mercury amalgam and the square root of the ratio of the diffusion coefficient of the metal in the amalgam to the diffusion coefficient of the ion in solution. This postulate cannot be accepted since the condition of diffusion to the dropping mercury electrode differs considerably from the conditions assumed by Randles.

From Table 1 it follows that with an increasing rate of saw-tooth voltage change the maximal current of the reduced ion increases. In carrying out quantitative analysis, therefore, the rate of voltage change must be standardized.

Effect of the Amplitude of the Saw-tooth Voltage on the Dropping Period of the Mercury Electrode.

It is known that when a negative potential is applied to a cell the drop time (t) of the mercury electrode changes according to the electrocapillary curve. We were interested in comparing the changes in dropping time for various saw-tooth voltages with t obtained on applying a fixed negative potential. A number of experiments were therefore carried out to give results which are shown graphically in Fig. 14. In all cases electrolysis was carried out in the absence of atmospheric oxygen.

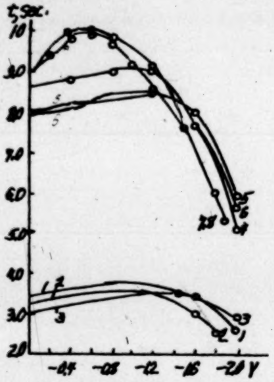

Fig. 14. Change in drop time of the mercury with the amplitude of the saw-tooth voltage.

The amplitude of the saw-tooth voltage and the drop time in seconds (t) are plotted along the abscissa and ordinate respectively. Curves 1,2 and 3 Fig. 14 represent electrocapillary curves obtained in 0.1 N KCl, $5 \cdot 10^{-4}$ M $CdCl_2$ in 0.1 N KCl and $5 \cdot 10^{-4}$ M $CdCl_2 + 5 \cdot 10^{-4}$ M $ZnCl_2$ in 0.1 N KCl.

On comparing these curves it is not difficult to observe that the electrocapillary curve for 0.1 N KCl is higher than curves 2 and 3. The elctrocapillary maximum is shifted to more negative values of the saw-tooth voltage in all cases. Considerable changes in the drop time are observed beginning with a saw-tooth voltage amplitude of 1.2 V relative to the saturated calomel electrode. Curves 4,5,6,7, and 8 were obtained with a slow drop time. Curves 4, 5, and 6 correspond to electrocapillary curves obtained in 0.1 N KCl, 10^{-4} M $CdCl_2$ in 0.1 M KCl and 10^{-4} M $ZnCl_2$ in 0.1 N KCl, respectively. Curves 7 and 8 were obtained in 0.1 N KCl and 10^{-4} M $CdCl_2$ in 0.1 N KCl on applying a constant negative potential to the cell.

A comparison of these curves shows that curves 7 and 8 are somewhat higher than curves 4 and 5, while the electrocapillary maxima on curves 7 and 8 are located at a negative potential of -0.56 V relative to the saturated calomel electrode, while the maxima in 5 and 6 are displaced to even more negative values of $V_{\sim}$.

When electrolysis is carried out using a slow drop time, the changes in the drop time which begin at $V_{\sim} = 1.2$ V are considerably greater than in the case of a capillary with a drop time of ca. 3 sec. (compare curves 4,5, and 6 with curves 1, 2, and 3, Fig. 14).

Since the amplitude of the saw-tooth voltage does effect the drop time, it is necessary (when taking oscillograms) in carrying out quantitative analysis to specify the drop time at a given value of the applied voltage $V_{\sim}$.

Quantitative Determination of Certain Ions.

Since it has been shown that the rate of change of the saw-tooth voltage and the effective pressure on the dropping mercury affect the value of the maximal current of the reduced ion, we used steady values for v and for the pressure on the dropping mercury. Electrolysis was carried out in the absence of atmospheric oxygen. The results are given in Tables 2, 3, 4, and 5.

TABLE 2

Maximal current values for various cadmium concentrations in 0.1 N KCl $m = 2.6$ mg/sec; $t = 3.5$ sec; $\nu = 10$ sweeps/second; $\underline{v} = 18$ V/sec; $h = 280$ mm

Cadmium concentration in mols/liter	Maximal current in μA
10^{-3}	223.0
$5 \cdot 10^{-4}$	115.0
10^{-4}	23.0
$5 \cdot 10^{-5}$	11.7
10^{-5}	2.42
$5 \cdot 10^{-6}$	1.38
10^{-6}	0.31

TABLE 3

Maximal current values for various cadmium concentrations in 0.1 N KCl $m = 0.76$ mg/sec; $t = 8.28$ sec; $\nu = 7.5$ sweeps/second; $\underline{v} = 13.77$ V/sec; $h = 470$ mm

Cadmium concentration in mols/liter	Maximal current in μA
10^{-4}	19.1
$5 \cdot 10^{-5}$	9.75
10^{-5}	2.04
$5 \cdot 10^{-6}$	1.08
10^{-6}	0.24

It is clear from Table 2 that there is a linear relation between maximal current and cadmium concentration. There is a slight deviation from linearity when the solutions are very dilute.

The sensitivity of the oscillographic method is considerably higher than that of the ordinary polarographic method, since the latter can only determine 10^{-5} M $CdCl_2$ even when multi-capillary electrodes are used. An ordinary polarogram for 0.1 N KCl containing 10^{-5} M $CdCl_2$ is shown in Fig. 15 as an example. Two capillaries with differing drop times were used to get this curve. The volume of the test solution was 25 ml. A cadmium wave is clearly discernible on this curve but the limiting current of the cadmium has only a small plateau. Following after the cadmium curve there is an appreciable supplementary current which is caused by the tangential movement of the mercury surface and by the shearing off of drops.

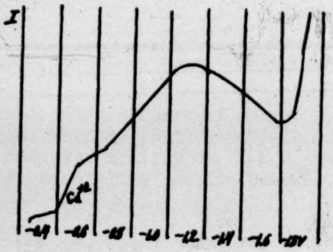

Fig. 15. Polarogram for cadmium chloride in 0.1 N KCl.

On halving the cadmium concentration of the last experiment a clear-cut wave for cadmium is no longer discernible since it fuses into the supplementary current. It is not possible therefore to determine concentrations of cadmium of the order of $5 \cdot 10^{-6}$ M $CdCl_2$ by ordinary polarography even when using a multi-capillary set-up. By the oscillographic method, however, it is possible to get a reduction curve for cadmium on the screen even for a concentration of 10^{-7} M $CdCl_2$ in 0.1 N KCl.

Table 3 contains results for the maximal current obtained with a slow drop time.

These results show that when a slow drop time is used, there is linear relation between the concentration of the reduced ion and its maximal current.

Table 4 contains results for zinc.

TABLE 4

Maximal current values for various concentrations of zinc in 0.1 N KCl
$m = 2.6$ mg/sec; $t = 3.2$ sec; $\nu = 10$ sweeps/second; $\underline{v} = 18$ V/second;
$h = 280$ mm

Zinc concentration in mols/liter	Maximal current in μA
10^{-3}	235.0
$5 \cdot 10^{-4}$	120.0
10^{-4}	24.0
$5 \cdot 10^{-5}$	12.4
10^{-5}	2.61
$5 \cdot 10^{-6}$	1.46
10^{-6}	0.35

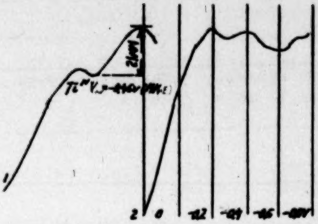

Fig. 16. Oscillogram and polarogram for Ti(IV) in the presence of iron and vanadium.

The results in Table 4 show that there is a linear relation between maximal current and zinc concentration; the curve deviates slightly from linearity on going toward low concentrations. The maximal current for zinc is somewhat higher than that of cadmium (compare the results of Tables 2 and 4).

Results given in Table 5 illustrate the effect of one ion on the maximal current of another when both are present together in 0.1 N KCl Solution.

TABLE 5

Maximal Current for Various Concentrations of Cadmium and Zinc in 0.1 N KCl

$m = 2.6$ mg/sec; $t = 3.2$ sec; $\nu = 10$ sweeps/second; $\underline{v} = 18$ V/sec; $h = 280$ mm;

$$\frac{c_{Cd}}{c_{Zn}} = 1$$

Concentration of cadmium and zinc in mols/liter	Maximal current in μA	
	Cadmium	Zinc
10^{-3}	250.2	163.8
$5 \cdot 10^{-4}$	126.8	84.48
10^{-4}	25.92	17.55
$5 \cdot 10^{-5}$	13.48	9.15
10^{-5}	2.73	1.92

It follows from Table 5 that when zinc and cadmium both occur simultaneously in a test solution the linear relation between concentration and maximal current for both Cd^{2+} and Zn^{2+}, respectively, is maintained within the limits of the experimental error of ordinary polarography. A comparison of the results given in Tables 2, 4, and 5 shows that the zinc ion increases the value of the cadmium maximal current to a value greater than that obtained, I_{max}, when Zn^{2+} is absent. The cadmium ion decreases the maximal zinc current to a value less than I_{max} when cadmium is absent.

Fig. 8 represents an oscillogram obtained when both cadmium and zinc ions were present together in solution. The maximal current of Cd^{2+} is considerably greater than the maximal Zn^{2+} current. The results in Table 5 show that the oscillographic method is a suitable one for investigating the effect of one ion on another as well as for the quantitative analysis of dissolved substances.

As an example of the superiority of the oscillographic polarograph over the ordinary polarograph we have adduced the results of an experiment on the determination of quadrivalent titanium in the presence of trivalent iron and quinquevalent vanadium.

The two curves given in Fig. 16 were obtained in 1 N H_2SO_4 saturated with sodium oxalate; 1 ml of solution contained 10 γ Ti(IV) , 100 γ V(V) and 250 γ Fe^{3+} The first curve is an oscillographic curve on which a titanium wave is clearly defined, while no titanium wave can be observed on the second curve, which was obtained by means of ordinary polarography; in the latter case the titanium wave has fused into the wave of trivalent iron and quinquevalent vanadium. On Fig. 16 $V_{\sim}$ is the amplitude of the saw-tooth voltage at which titanium is reduced on the dropping mercury cathode.

SUMMARY

1. A first model of an oscillographic polarograph has been constructed by means of which microanalysis of solutions can be carried out.

2. The effect of the rate of potential change on the value of the maximal current of the reduced ion has been studied.

3. The effect of the amplitude of the saw-tooth voltage on the drop time of the mercury electrode has been studied.

4. It has been shown that the linear relation between the value of the maximal current of a reduced ion and its concentration in solution only holds when the rate of potential change and the effective pressure on the dropping mercury remain constant.

5. It has been shown that by means of the oscillographic polarograph constructed it is possible to determine a test ion in concentrations of 10^{-8} mol/liter.

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THE APPLICATION OF COMPLEXONES IN POLAROGRAPHY

1. DETERMINATION OF TITANIUM

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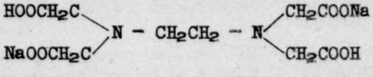
Zeltzer [1], has shown that titanium (IV) gives a reduction wave in weak acid solution at a potential of -0.81 V relative to the saturated calomel electrode. This wave is the result of the process Ti (IV) + e → Ti(III).

Nevertheless, according to the results of other investigators [2], as well as ourselves, the Ti (IV) wave obtained in acid solution is poorly defined and is not suitable for quantitative determination of titanium. This is the result chiefly of the irreversibility of the process as shown by Strubl [2], (because the oxidation of titanium (III) occurs at a potential of -0.18 V) and the rather extended wave obtained fuses with the hydrogen ion wave. Complexing agents are therefore used for the polarographic determination of titanium. It has been shown that by complexing Ti (IV) with tartrate, citrate [2], thiocyanate [3], and oxalate [4], clearly defined waves are obtained which correspond to the reversible process Ti (IV) $\rightleftarrows$ Ti (III), during which the reduction potential if shifted to more positive values. E.g., for tartaric acid and citric acid this potential is -0.48 V.

Zanko and co-workers developed a method of determining titanium in bauxite, kaolin, slags, [5], casts and steels [6] in which tartaric acid was used as a complexing agent; he showed that for the determination of titanium in casts and steels in 14% tartaric acid solution, after preliminary reduction of iron (III) with aluminum dust, the method which is based on a calculating technique has an error of 4-5% for a titanium content of 0.4 - 1%. A 1 M tartaric acid solution in 0.5 M sulfuric acid has also been used for polarographic determination of titanium in clays, granites, syenites and other minerals and in ores [7]. In this solution the half-wave potential is -0.3 V against the saturated calomel electrode.

Under these conditions titanium can be determined in the presence of Al, Zr, Th, Nb, Ta, the alkali and the alkaline earth elements. Fe, Cu, and Cr are precipitated first on the mercury cathode. Only uranium interferes. Titanium has been determined in clays [4], using sodium oxalate in 1 N sulfuric acid as supporting electrolyte, the solution also contains 8% urea for maximum suppression. According to the author iron does not interfere under these conditions. It has been shown [8], that the half-wave potential of titanium in this supporting electrolyte does not depend on the concentration of titanium and iron.

We used Trilon B which is the disodium salt of ethylenediaminetetracetic acid as the complexing agent for the polarographic determination of titanium



$$\begin{array}{l} HOOCH_2C \\ \end{array}\!\!\!\!\!\!\begin{array}{c} \\ \end{array} HOOCH_2C,\ NaOOCH_2C > N - CH_2CH_2 - N < CH_2COONa,\ CH_2COOH$$

Trilon B is also know as "Complexone III", 'Versene" etc.

This reagent forms very stable complexes with many metals and is finding ever increasing application in chemical analysis for the determination of many metals [9].

Trilon B is a white crystalline material which is comparatively soluble in water but practically insoluble in acids. According to our observations the salt hardly dissolves at all at a pH of ca. 2.

Complexones have hitherto only found limited application in polarography; nevertheless the fact that they form complexes which strongly displace the reduction potentials of many metals, may open up many new possibilities for the determination of metals when these are present simultaneously.

E.g., is has been shown that by using Complexone III it is possible to determine cobalt in the presence of nickel and other metals, if the cobalt is first of all oxidized to Co(III), and also to determine iron in the presence of a large excess of copper [10].

Polarographic methods involving the use of Complexone III have also been suggested for the determination of thallium in the presence of lead and tin [11], molybdenum in the presence of tungsten [12], and uranium in the presence of chromium, titanium, etc., [13].

The effect of pH on the displacement of the reduction or oxidation potentials of the complexes of several cations with Complexone III has been investigated [14].

EXPERIMENTAL

Measurements were made with a Heyrovsky automatic-registering polarograph with a galvonometer sensitivity of 2.21×10^{-9} A/mm. The electrolyzer was connected to a saturated calomel electrode serving as anode by means of an agar-agar bridge. All the potentials given in this article are relative to the saturated calomel electrode.

The capillary had the following characteristics $m^{2/3} t^{1/6} = 1.434$ $mg^{2/3}$ $sec^{-1/2}$ in a 1 N solution of KCl-0.05 N HCl at -0.8 V. The cell was thermostated at 25 ± 0.5°. pH's were measured with an LP-4 vacuum tube voltmeter and universal indicator (for coarser measurements).

The following solutions were used:

1. A stock solution of titanium sulfate was prepared by treating potassium fluorotitanate three times in succession with sulfuric acid with heating till evolution of sulfuric acid vapors. The cooled solution was made up to standard volume with water. The titanium content of the solution was determine gravimetrically as TiO_2 after precipitation with ammonia. 1 liter contained 1.8682 g TiO_2. Solutions of lower concentration were made from the stock solution by dilution with 5% sulfuric acid.

2. 0.3 M solutions of Trilon B in water or 0.1 M in 2 M sodium acetate were prepared after recrystallization of Trilon B from water.

3. A solution of 2 M sodium acetate.

4. Redistilled acids.

The Polarographic Characteristics of the Complex formed between Titanium and Trilon B.

Titanium forms a complex with Trilon B at certain pH's which is reduced on the dropping mercury cathode to give a well defined wave with a half-wave potential which depends on the pH.

Curves 1 and 2 (Fig. 1) were obtained with a solution which was 1.17mM with respect to titanium and 0.1 M and 2 M, respectively, with respect to Trilon B and sodium acetate, the pH was ca. 5.

The half-wave potential at this pH was -0.473 V. Analysis of this wave by means of the Heyrovsky-Ilkovich equation

$$E_{c.e.} = E_{1/2} - \frac{0.0591}{n} \log \frac{i}{i_d - i}$$

gave a slope of 0.062 V on constructing a graph; his is in good agreement with the theoretical value of 0.059 for an unielectron process. This indicates that the reduction of the complex titanium ion is reversible and proceeds according to the following scheme

$$\mathrm{Ti\ (IV)} + e \rightleftarrows \mathrm{Ti\ (III)}.$$

Titanium is also reduced in a solution of sodium acetate (2 M) in the absence of Trilon B to give a wave with a half-wave potential of ca. -1 V; this wave however is extended and does not have a clear-cut plateau for the limiting current (Curve 3, Fig. 1).

Effect of pH on the Titanium Half-Wave Potential.

The effect of pH on the half-wave potential of the titanium complex was also studied. Solutions were prepared which were 0.468 mM, 0.1 M, and 2 M respectively, with respect to titanium, Trilon B, and sodium acetate; the pH was varied.

The pH was altered by addition of either sulfuric acid or ammonia. The results obtained are given in Fig. 2 and Table 1

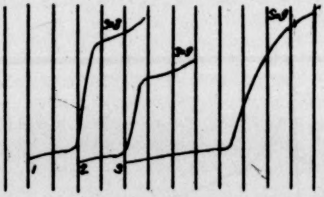


Fig. 1. Curves 1 and 2 - 1.17 mM solution of titanium in a supporting electrolyte of 0.1 M Trilon B and 2 M sodium acetate, pH ca. 5; Curve 3 - 1.17 mM solution of titanium in a supporting electrolyte of 2 M sodium acetate.

TABLE 1

pH of solution	$E_{1/2}$ in V against the saturated calomel electrode.
5.50	- 0.555
4.60	- 0.427
3.40	- 0.418
2.25	- 0.391
0.80	Wave distorted

The results in Table 1 show that the pH has a considerable effect on the half-wave potential of the titanium complex. At low pH's the half-wave potential shifts to the positive side while at very low PH, the complex decomposes.

This indicates that the stability of the titanium complex decreases with decreasing pH. At high pH's the Trilon B does not protect titanium from hydrolysis and as a consequence no titanium wave is obtained. This agrees with Przhibil's results [9], and indicates that although the complexone strongly inhibits the separation of titanium hydroxide, the latter can be precipitated quantitatively on long standing (ca. 5 hours). For quantitative polarographic determination of titanium, therefore, it is best to use a solution possessing buffer activity as the supporting electrolyte. For this purpose we used a 2 M solution of sodium acetate having a pH of 4.5-5.0.

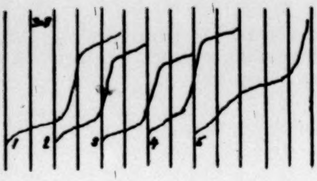
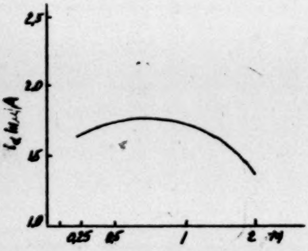


Fig. 2. Effect of pH on the half-wave potential of the titanium complex: 0.468 mM solution of titanium in a supporting electrolyte of 0.1 M Trilon B and 2 M sodium acetate for various pH values: 1) 5.50; 2) 4.60; 3) 3.40; 4) 2.25; 5) 0.80.

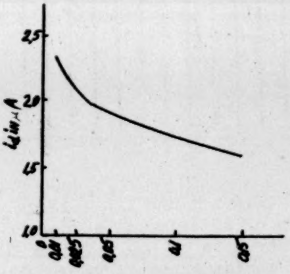
Effect of Sodium Acetate and Trilon B Concentrations, Respectively, on the Half-Wave Potential and on the Value of the Diffusion Current.

During a study of the effect of sodium acetate concentration, it was found that the half-wave potential of the titanium complex hardly changes at all with changes in sodium acetate concentration when the pH was kept constant. The diffusion current decreases slightly with increasing sodium acetate concentration, starting at a concentration of 0.5 N sodium acetate, as shown in Fig. 3 for a 0.468 mM solution of titanium which was also 0.1 M with respect to Trilon B and had various concentrations of sodium acetate. The Trilon B concentration does not affect the half-wave potential of the titanium complex when the pH is kept constant, the diffusion current decreases slightly with increasing Trilon B concentration (Fig. 4).



Sodium Acetate Conc.

Fig. 3. Effect of sodium acetate concentration on the value of the diffusion coefficient of titanium. 0.468 mM of titanium in 0.1 M Trilon B as supporting electrolyte.



Trilon B conc. in M

Fig. 4. Effect of Trilon B concentration on the value of the diffusion current of titanium. 0.468 mM solution of titanium in 0.2 M of sodium acetate as base electrolyte.

All further measurements were therefore made in 2 M sodium acetate which is 0.1 M with respect to Trilon B, since it is obvious from the polarograms obtained under these conditions, that the limiting current is the optimum.

Determination of the Diffusion Current Constant.

The diffusion current constant was determined by carrying out measurements in 2 M sodium acetate which was 0.1 M with respect to Trilon B and containing titanium in concentrations varying from 2.34 · 10^{-4} - 2.34 · 10^{-3} M, and also in the supporting electrolyte alone. The results obtained are given in Table 2 and Fig. 5.

TABLE 2

Ti taken in mM/l	i_d μA obtained	i_d μA found after correction for residual current.	$K = i_d/c$ μA /mM/liter	Deviation of K, in % of the mean
-	0.238	-	-	-
0.234	0.953	0.715	3.05	-3.93
0.468	1.718	1.480	3.16	-0.31
0.936	3.068	2.830	3.02	-4.75
1.404	4.859	4.621	3.29	+3.93
2.340	8.060	7.822	3.34	+5.09
		Mean . . .	. 3.17 ± 0.11	

These results show that the diffusion current constant varies from 0.31-5% of the mean value which signifies that a linear relation exists between the diffusion current and the concentration of titanium in solution for the concentrations studied, viz. 2.34 · 10^{-4} – 2.34 · 10^{-3} M/liter. At high titanium concentrations (ca. 2mM/liter) a maximum is observed on the curve.

Effect of the Order in which Reagents are Added.

We showed that the order in which the reagents are added has an essential effect on the value of the titanium diffusion current. If the sodium acetate is added first to the test solution of titanium, and the Trilon B added subsequently, the diffusion current is lowered considerably. This is the result apparently of the fact that the titanium forms a complex with the sodium acetate which reacts slowly with the Trilon B. This is confirmed by Curve 1, Fig. 6 which was obtained with 0.468 mM of titanium solution when 1 M sodium acetate was added first, followed by Trilon B to 0.05 M.

Curve 2 on the same diagram represents what happens to a solution of the same titanium concentration when the titanium solution is added to a 1 M solution of sodium acetate containing Trilon B at a concentration of 0.05 M. It is necessary, therefore, to use a solution of sodium acetate containing Trilon B as reagent. In this case the order of addition of the reagent is of no significance.

Effect of Iron, Vanadium, Copper and Chromium.

The effect of iron, vanadium, copper and chromium on the polarographic determination of titanium as its complex with Trilon B was investigated. Iron (III) gives a complex with Trilon B in 2 M sodium acetate which is reduced at a potential of -0.12 V, i.e. at a potential which is 0.35 V more positive than the half-wave potential of titanium. Therefore iron in amounts which are 4-5 times that of titanium does not interfere with the titanium diffusion current as is evident from Curves 1 and 2 of Fig. 7. When, however, large amounts of iron are present, exact determination of titanium becomes impossible. The reduction of iron (III) to iron (II) by various reducing agents (hydrazine sulfate, ascorbic acid) leads to a partial reduction of titanium also, both by the reducing agents themselves and by the iron complexes (II) formed, which possess strong reducing powers [15]. When, therefore, large amounts of iron are present, it is necessary to remove it by electrolytic precipitation on a mercury cathode or to separate the titanium by precipitating with ammonia after complexing the iron and titanium with Trilon B. Under these conditions, iron (III) is not precipitated by ammonia, while titanium is precipitated quantitatively on long standing (ca. 5 hours) [9].

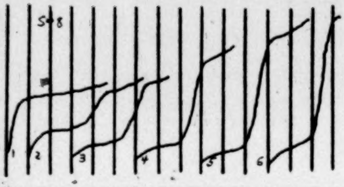


Fig. 5. Polarograms for titanium at different concentrations in a supporting electrolyte of 0.1 M Trilon B in 2 M sodium acetate.

1- Supporting electrolyte; 2- 0.234; 3- 0.468; 4- 0.702; 5- 0.936; 6- 1.170 mM titanium.

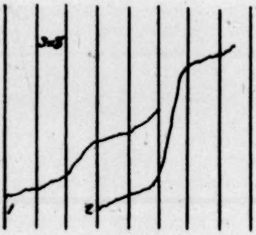


Fig. 6. Effect of the order of addition of the reagents. 0.468 mM of titanium in a supporting electrolyte of 0.05 Trilon B and 2 M sodium acetate.

1- sodium acetate is first added to the titanium solution followed by Trilon B; 2- the titanium is added to sodium acetate containing Trilon B.

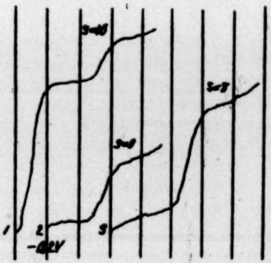


Fig. 7. Effect of iron (III) and chromium (III) on the titanium diffusion current:

1- 22.4 µg of titanium and 75 µg of iron (III) per ml in a supporting electrolyte of 0.1 Trilon B and 2 M sodium acetate; i_d = 1.4 µA; 2- the same solution; polarographing started at 0.2 V; 3- 22.4 µg titanium in 1 ml and 100 µg of chromium (III) in 1 ml, in the same supporting electrolyte; i_d = 1.50 µA.

Vanadium (V) has a considerable effect on the value of the diffusion current of the titanium complex and increases it. On reduction to vanadium (IV) with hydrazine sulfate its effect is not eliminated; vanadium must therefore be removed before determining titanium polarographically.

Copper also interferes since it forms a complex with Trilon B which is reduced on the dropping mercury electrode at a potential near to that for titanium; the half-wave potential of the complex with Cu^{2+} is -0.4 V.

It is essential, therefore, to remove copper as well before determination of titanium with Trilon B. Chromium (III) has practically no effect on the value of the titanium diffusion current (Curve 3, Fig. 7).

Results are given in Table 3 which illustrate the effect of the elements mentioned above, which are of varying valencies, on the diffusion current of the titanium complex with Trilon B.

TABLE 3

Metals taken in μg/ml.						i_d μA found	Observations
Ti(IV)	Fe(III)	Fe(II)	V(V)	V(IV)	Cr(III)		
22.4	-	-	-	-	-	1.48	Fe (III) and V(V) were reduced either by heating with hydrazine sulfate, or with ascorbic acid at room temperature.
44.8	-	-	-	-	-	2.98	
22.4	75.5	-	-	-	-	1.40	
22.4	-	500	-	-	-	1.00	
22.4	-	-	100	-	-	2.17	
44.8	-	-	125	-	-	4.25	
22.4	-	-	-	500	-	7.34	
56.0	-	500	-	250	-	5.00	
22.4	-	-	-	-	50	1.50	
22.4	-	-	-	-	100	1.55	

SUMMARY

1. It has been shown that the complex of titanium with Trilon B is reduced reversibly on the dropping mercury cathode.

2. The effect of pH on the half-wave potential of the complex formed between titantium (IV) and Trilon B has been studied.

3. The effect of the concentrations of Trilon B and sodium acetate on the half-wave potential and the diffusion current of the complex formed between titanium (IV) and Trilon B has been studied.

4. The effect of iron (III) and (II), vanadium (V) and (IV), copper (II), and chromium (III) on the polarographic determination of titanium with Trilon B has been investigate.

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POTENTIOMETRIC TITRATION WITH THE FERRI-FERROCYANIDE ELECTRODE

DETERMINATION OF COPPER

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Of a number of attempts to develop a potentiometric method for copper based on the use of ferrocyanide solutions only two seem to have been successful [1,2].

From published data it is known that the composition of copper ferrocyanide does not correspond to the formula $Cu_2Fe(CN)_6$ but depends on the experimental conditions [1,2,3].

In order to get a precipitate of constant composition the following may be added:

1. A strong electrolyte which is indifferent [3], or which reacts with the ferrocyanide ion [1], or

2. A complexing agent which gives a soluble complex with Cu^{2+} [2].

The combined use of 1 and 2 is also possible [3].

In our opinion the increase in ionic strength in the first case is sufficient to ensure that the activity coefficient of the titrated ion is small enough and remains practically constant during the whole of the titration; this consequently ensures a constant composition for the precipitate.

Of course in some reactions one must take into account the common ion effects, the coagulative action of electrolytes and also increases in precipitates solubility.

In the second case, i.e. 2 above, it is our opinion that a complexing agent which gives a soluble complex with Cu^{2+} maintains a small and practically constant concentration of Cu^{2+} ions during the whole of the titration thereby determining the instability constant of the given soluble complex; this ensures the formation of a copper ferrocyanide of constant composition (in view of the low Cu^{2+} concentration it may be assumed that the activity coefficient is equal to 1; we do not take into account the fact that in aqueous solution it is the aquocomplexes which are present and not the free Cu^{2+} ions).

There is of course no basis for considering that the methods described for getting precipitates of constant composition are confined only to ferrocyanides.

Existing ferrocyanide methods for potentiometric titration of copper [1,2] have not been worked out in sufficient detail; we have therefore tried to find new variants.

EXPERIMENTAL

We used a compensation set-up. A platinum disc ca. 0.4 cm^2 was used as reference electrode. A saturated calomel electrode was used as the auxiliary electrode; the null-instrument was a needle galvanometer ($1^\circ = 0.26 \cdot 10^{-6}A$), the electrolytic bridge was a siphon filled with a saturated solution of potassium chloride, the ends being stopped with porous plates.

Preliminary experiments showed that to get a copper ferrocyanide of constant composition the best complexing agent was ammonium hydroxide; this agrees with Kale's results [2]; glycerol and ammonium oxalate are reasonably satisfactory complexing agents.

The results are not reproducible when Rochelle salt is used. On neutralization with sodium hydroxide of the acid formed by substitution of the hydrogen of the hydroxyl groups of this salt with Cu^{2+} ions, no precipitate of copper ferrocyanide is obtained at all. This can probably be explained on the assumption that an inner complex compound of copper is formed in alkaline media and this complex, which is very stable, is not decomposed by the ferro-cyanide.

Ammoniacal, oxalate, and glycerol complexes of copper are sufficiently unstable to be decomposed by ferrocyanide and moreover regulate the copper ion concentration by acting as buffers with respect to the copper.

This property, in our opinion can best be evaluated by calculating the ratio of the copper ion concentration of the given soluble cupri-complex $[Cu^{2+}]_c$ to the copper ion concentration which is determined by the solubility of the precipitate of cupric ferrocyanide formed $[Cu^{2+}]_{ppt}$.

$[Cu^{2+}]_c$ for the oxalate complex was calculated from $\frac{[Cu^{2+}]\,[C_2O_4{}^{2-}]^2}{[Cu(C_2O_4)_2^{2+}]} =$

$= 6 \cdot 10^{-6}$ [4], the concentration of the $CuSO_4$ solution was = 0.05264 mol/liter;

while $[Cu^{2+}]_{ppt}$ for the cuprammonium complex was calculated from $\frac{[Cu^{2+}]\,[NH_3]^4}{[Cu(NH_3)_4^{2+}]} =$

$= 2.1 \cdot 10^{-13}$ [4], the concentration of the $CuSO_4$ being 0.04753 mol/liter.

In both cases $[Cu^{2+}]_{ppt.}$ was assumed to be equal to $2.5 \cdot 10^5$ g-ion/liter while the concentration of the non-dissociated part of the complex was assumed to be equal to the $CuSO_4$ concentration.

Approximate calculations of the ratio $[Cu^{2+}]_c : [Cu^{2+}]_{ppt.}$ in the case where ammonium hydroxide was used gave a value of 21, while the ratio for the oxalate complex was ca. 17 (we could not find any published data on the instability constant of the copper glycerol complex).

One would expect therefore that the "buffer" action mentioned above will be shown by all soluble complex copper compounds for which the ratio $[Cu^{2+}]_c : [Cu^{2+}]_{ppt.}$ is of the order of 20.

For accurate work, analytical quality reagents were recrystallized from twice-distilled water before use.

$CuSO_4$ solutions were standardized electrolytically. 0.2-0.4 M solutions of $K_4Fe(CN)_6$ were prepared from weighed amounts of $K_4Fe(CN)_6 \cdot 3H_2O$ kept in a desiccator over fused NaBr. The empirical titer of the potassium ferrocyanide with respect to copper was established by the potentiometric method described below.

The molarity of the $K_4Fe(CN)_6$ solution was determined volumetrically by titration with 0.1 N $KMnO_4$ in one case, the latter having been standardized with crystalline sodium oxalate. ca. 0.5 N solutions of Na_2HAsO_3, Na_2HAsO_4 and a 25% solution of ammonia were also among the reagents employed. $Na_2S_2O_3$ was standardized against potassium bichromate.

Copper was titrated in ammoniacal solution as follows: To a known volume of $CuSO_4$ solution continuously stirred with a mechanical stirrer, was added from a buret ammonium hydroxide until the turbidity of $Cu(OH)_2$ just disappeared; this point was checked by observation in the light of an electric lamp. After addition of a few drops of ca. 0.5 M $K_3Fe(CN)_6$, the solution was titrated with $K_4Fe(CN)_6$; after addition of the aliquots of $K_4Fe(CN)_6$ to the titration flask, the whole was mixed for 2 (or 1) minutes; the stirrer was then switched off and the solution allowed to stand for 2 (or 1) minutes and the compensation point determined.

The maximal value of the potential jump $\Delta E/\Delta V$ was accepted as the respective equivalence point.

The following should be noted: ammonium hydroxide is a suitable complexing agent for another reason, viz. because the cupric ferricyanide is soluble in it while the ferrocyanide is not, even when excess NH_4OH is present; thus, when 0.09290 g of Cu^{2+} in 47 ml was taken and 0.6 ml of 25% ammonium hydroxide added in excess, and the solution titrated with $K_4Fe(CN)_6$ to the equivalence point, no Cu^{2+} could be detected qualitatively in the centrifugate after removal of the copper ferrocyanide precipitate.

We found that the time necessary for stirring the solution during titration and also for letting the solution stand before finding the compensation point may be either 2, or 1 minute each, without sacrificing the accuracy of titration.

By increasing the rate of addition of the working solution the total time for titration can be reduced from 120 to 20 minutes without decreasing the accuracy of the determination; when the time taken is 20 minutes, equilibrium reactions are only established near the equivalence point.

We titrated equal amounts of copper with two $K_4Fe(CN)_6$ solutions of equal molarity (0.2000) prepared at different times from separate aliquots of the salt; and further, using the empirical titrations of these solutions with respect to copper, carried out quantitative determination of copper.

The results obtained are given in Table 1; the errors in both cases are within the limits of experimental error.

TABLE 1

Titration of Cu^{2+} with 0.2 M solutions of $K_4Fe(CN)_6$ prepared at different times

Cu taken, in g	Cu found by titration with $K_4Fe(CN)_6$ T = 0.02569 Cu, in g	Relative error (%)	Cu found by titration with $K_4Fe(CN)_6$ T = 0.02621 Cu, in g	Relative error (%)
0.1162	0.1161	−0.09	0.1172	+0.86
0.1162	0.1165	+0.26	0.1179	+1.16
0.1162	0.1163	+0.09	0.1158	−0.34
0.1162	0.1154	−0.67	0.1160	−0.17
0.1162	0.1155	−0.60	0.1173	+0.95

It is only necessary, therefore, to standardize the $K_4Fe(CN)_6$ once with copper, and then to prepare further $K_4Fe(CN)_6$ solutions of the same concentration by weighing out the same weight of dry salt as used in making up the standardized solutions.

The composition of the precipitate does not correspond to the simple formula $Cu_2Fe(CN)_6$; this was confirmed by the results given below.

On the basis of the amount of potassium ferrocyanide used during potentiometric titration of a known amount of copper, we calculated the ratio of the number of molecules of $CuSO_4$ to $K_4Fe(CN)_6$ corresponding to the composition of the precipitate. We used the molarity of the potassium ferrocyanide calculated from the weight of salt used. The mean value of the ratio was found to be 2.043. This can probably be explained by the presence of a small amount of basic copper salts in the precipitate.

TABLE 2

Titration of various amounts of Cu^{2+} at various dilutions

$CuSO_4$ solution used, in ml	Molarity of the $CuSO_4$ solution	Cu taken, in g	H_2O added, in ml	$K_4Fe(CN)_6$ used, in ml	$T_{\frac{K_4Fe(CN)_6}{Cu}}$	Cu found, in g	Relative error (%)
9.98	0.07320	0.04645	18	1.777	0.02621	0.04658	+0.28
9.98	0.07320	0.04645	18	1.769	0.02621	0.04636	-0.19
9.98	0.07320	0.04645	30	1.773	0.02621	0.04647	+0.04
9.98	0.07320	0.04645	30	1.761	0.02621	0.04615	-0.65
24.96	0.07320	0.1162	25	4.429	0.02621	0.1161	-0.09
24.96	0.07320	0.1162	25	4.444	0.02621	0.1165	+0.26
24.96	0.1464	0.2324	20	4.473	0.05189	0.2321	-0.13
24.96	0.1464	0.2324	50	4.487	0.05189	0.2329	+0.21
24.96	0.1464	0.2324	87	4.473	0.05189	0.2321	-0.13
24.96	0.1464	0.2324	87	4.467	0.05189	0.2318	-0.26

TABLE 3

Titration of Cu^{2+} in the presence of NH_4NO_3

Cu taken, in g	Volume titrated, in ml	NH_4NO_3 added, in g	$K_4Fe(CN)_6$ used, in ml	$T_{\frac{K_4Fe(CN)_6}{Cu}}$	Cu found, in g	Relative error (%)
0.04645	28.6	0.07	1.776	0.02620	0.04656	+0.24
0.04645	28.6	0.1	1.772	0.02605	0.04616	-0.62
0.04645	29.2	0.3	1.792	0.02605	0.04669	+0.52
0.04645	20.5	0.5	1.858	0.02620	0.04866	+4.76
0.04645	20.4	1.0	2.101	0.02620	0.05501	+18.43
0.1162	52	0.25	4.457	0.02605	0.1161	- 0.09
0.1162	51.3	0.4	4.465	0.02586	0.1155	- 0.60

We also calculated the molar ratios for the results given above with the exception that we used the molarity of $K_4Fe(CN)_6$ determined by volumetric permanganate titration.

In comparison with the ratio of 2.043 adduced above, the molar ratio of $CuSO_4:K_4Fe(CN)_6$ corresponding to the precipitate composition increased in these cases to an even greater value of 2.147; we are inclined to ascribe this to the fact that something like less than 3 molecules of water of crystallization enters into the composition of the dry potassium ferrocyanide.

Table 2 contains the results of titrations of various amounts of copper at different dilutions. Within the limits indicated in Table 2, the results can be regarded as satisfactory.

Table 3 contains the results of titrations of copper in the presence of various amounts of an ammonium salt. The results are satisfactory up to the limiting concentrations of NH_4NO_3 used (See Table 3).

We are inclined to explain this by an increase in the solubility of the precipitate under the influence of NH_4 (displacement of the equilibrium toward the formation of NH_4OH at the expense of basic copper salts).

TABLE 4

Titration of Cu^{2+} in the presence of arsenic

Cu taken, in g	Volume titrated, in ml	As added, in g	$K_4Fe(CN)_6$ solution used, in ml	$T_{K_4Fe(CN)_6/Cu}$	Cu found, in g	Relative error (%)
0.04417	19.5	0.10 As^V	1.658	0.02620	0.04342	−1.70
0.04417	19.25	0.10 As^V	1.669	0.02620	0.04371	−1.04
0.04417	47.3	0.10 As^V	1.650	0.02620	0.04321	−2.17
0.04645	43.4	0.025 As^V	1.771	0.02605	0.04613	−0.75
0.04645	30.5	0.03 As^V	1.776	0.02620	0.04656	+0.23
0.04645	31.7	0.03 As^V	1.771	0.02620	0.04613	−0.75
0.04417	93	0.10 As^{III}	1.670	0.02620	0.04373	−0.99
0.04417	75.2	0.10 As^{III}	1.691	0.02620	0.04429	+0.27
0.04417	75.5	0.10 As^{III}	1.702	0.02620	0.04457	+0.90
0.04645	13.7	0.03 As^{III}	1.788	0.02605	0.04658	+0.28
0.04645	12.5	0.19 As^{III}	1.767	0.02605	0.04603	−0.90

Since determination of copper in the presence of arsenic – particularly in Paris Green $[3Cu(AsO_2)_2 \cdot Cu(CH_3COO)_2]$, is of practical interest, we carried out some initial titrations of copper in the presence of quinquevalent arsenic (Na_2HAsO_4). The results of these determinations are satisfactory, when the ratio of arsenic to copper does not greatly exceed the ratio in Paris Green (see Table 4).

Titration of copper in the presence of trivalent arsenic (Ne_2HAsO_3) was unsuccessful, probably because AsO_3^{3-} forms a stable compound with Cu^{2+} in alkaline media [5].

TABLE 5

Potentiometric determination of CuO in Paris Green

Wt. of Paris green, in g	$K_4Fe(CN)_6$ solution used, in ml $T_{K_4Fe(CN)_6/CuO}$ ~~0.03295~~	CuO found, in g	CuO content (%)
0.1667	1.671	0.05507	33.03
0.1667	1.662	0.05476	32.84
0.1667	1.664	0.05484	32.89
		Mean. . .	32.92

We got good results after oxidation of the AsO_3 by the following method. The weakly acid solution containing Cu^{2+} and AsO_3 to which had been added an excess of hydrogen peroxide was heated for 15-20 minutes on a water bath; in order to remove unreacted hydrogen peroxide the test solution was cooled, neutralized with sodium hydroxide using Tropeoline 00 as indicator, a 25% solution of ammonia (ca. 1.5 ml) was then added, and the test solution heated again for not more than 3 minutes (this is done in order to avoid separation of copper on the vessel walls as a dense precipitate which is soluble with difficulty in ammonium hydroxide.

After cooling. the test solution was titrated in an ammoniacal medium by the usual method (see Table 4).

Paris green was analyzed by dissolving ca. 5.00 g of it in 0.5 N HCl in a 300 ml standard flask. The solution was filtered and aliquots taken for oxidation of trivalent arsenic and subsequent determination of copper as described above (results are given in Table 5).

The same sample of Paris green was analyzed iodometrically [6]. The results given in Tables 5 and 6 are in good enough agreement for technical analysis.

TABLE 6

Iodometric determination of CuO in Paris Green

Wt. of Paris green, in g	$K_4Fe(CN)_6$ solution used, in ml $T_{K_4Fe(CN)_6/CuO} = 0.007823$	CuO found, in g	CuO content (%)
0.4168	17.60	0.1377	33.05
0.4168	18.00	0.1408	33.79
0.4168	17.80	0.1393	33.43
0.4168	17.50	0.1368	32.83
		Mean	33.27

SUMMARY

1. A method has been developed for the titration of copper in ammoniacal media with a solution of $K_4Fe(CN)_6$ using a ferri-ferrocyanide electrode.

2. Paris green has been analyzed by this method.

3. Attempts have been made to explain the reasons determining the constancy of the composition of copper ferrocyanide.

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A QUANTITATIVE X-RAY SPECTROGRAPHIC METHOD OF ANALYSIS

PART II

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In previous articles [1,2,3], the bases of certain new methods of X-ray spectrographic analysis have been put forward and ways of adapting them to practical use discussed.

In the present communication some of these general observations will be developed further and applied in particular to the analysis of the rare-earth group of elements, which is a classical object for the application of X-ray spectrographic methods. The rare-earths form a group of elements whose chemical properties are very similar. This is the reason for the difficulties which crop up in trying to separate and analyze them. At the same time this is also the reason why they can be fairly easily separated as a group from other elements. The exceptions are yttrium which follows the rare-earths and is usually considered in conjunction with them, scandium, and a few other elements which are sometimes present in small amounts in rare-earth concentrates. In those cases, therefore, where we are concerned with the determination of the content of individual rare-earths in samples where they are present to a considerable extent, the problem may easily be reduced to a quantitative X-ray spectrographic analysis of the individual elements of this group in concentrates containing the sum total of their oxides and a certain amount of other material which can be analyzed separately for yttrium and other elements. Having by some means of other determined either the total content of the rare-earths in the sample or the absolute content of one of them, it is then possible, instead of carrying out a direct quantitative determination of each of the rare-earths, to solve the problem by means of much simpler relative measurements which can be readily carried out with a reliable degree of accuracy. The technique of carrying out these measurements, upon which we have dwelt before [4], has undergone significant changes since that time, and at the present time [3], has been fairly thoroughly worked out. Thus, the analyst's problem can be reduced to the experimental determination of the combination of coefficients n_i in the relations $A_i = n_i A_o$, in which A_i is the content of the i'th rare-earth, while A_o is the content of the element which is taken as the arbitrary internal standard. In the case where the total content S of all the group of elements to be determined in the test sample is known, the final calculation of the sample's composition can be carried out by means of the equation:

$$A_i = \frac{n_i S}{\sum_{i=o}^{i=13} n_i}$$

in which $n_o = 1$.

Let us consider the experimental methods of determining the coefficients n_i which characterize the relative composition of the test mixture. In doing so, let us consider in parallel the two extreme cases – one, in which the test sample contains an appreciable quantity of all the elements comprising the rare-earth group or its fundamental subgroup, and the other where the sample contains only.

individual elements of the group considered which can be determined quantitatively 1) Although each of the methods described [3] is suitable for analyses in both cases, it is expedient to consider in particular under these conditions, those methods which are most convenient for solving the problem on hand. This should, in our opinion favor a more complete clarification, of the advantages and drawbacks of each of the analytical methods considered.

Analysis of Samples which Contain all the Elements to be Determined

In choosing X-ray spectrographic methods of analysis it is natural to prefer those which do not require the construction of a blackening curve.

Among the new methods which have been worked out recently and which belong to the group of "null" methods, which are independent of the shape of the blackening curve, may be included the method which is sometimes called the "spectral line width method" 2). Its basic principles have already been considered [3]. Here we shall only deal with the most important aspects. The shape of a large class of X-ray lines, to a first approximation, can be described by a dispersion formula, their width and arbitrary cross section can be calculated [8] by the formula:

$$x_n = \Gamma\sqrt{n-1}\,, \qquad (1)$$

where Γ is the so-called half-width of a line, while n is the ratio of the maximun intensity of the line (I_{max}) to the intensity at any point on the contour of the line (I). The width of the line calculated in this way which corresponds to a definite value of the ratio I_{max}/I, still remains unchanged on the contour of the line which has been deformed on account of the blackening curve, and which is registered on a photographic plate where the ratio between the true intensities of individual points along the contour has been destroyed 3). Having measured the width of one of the lines to be compared on the spectrogram at the height of maximum blackening of the other line, it is then possible by means of equation (1), independently of the form of function $S = S(I)$, to restore the true ratio of the intensity maximum of both lines, on the assumption that the shape of the emission line is not distorted by registration on a photographic plate. The ratio of the intensities of the two lines being compared when determined in this way is proportional to the ratio of the atomic content of the respective elements in the test mixture (ie. to the coefficient n_1 as used by us above).

Such is the practical method of determining the relative contents of the elements in the test material. However, in order that the method may be used effectively the following conditions must be followed: a) the lines being compared should be near one another; b) the background of each line should be identical. Otherwise when used, this method will come up against a number of difficulties, the necessity of overcoming which will detract considerably from the most important advantage of this method – its simplicity – and will lower its accuracy.

Both these conditions (a and b) are observed in the analysis of rare-earth concentrates containing all the elements. In such a case the fundamental lines of the test group of elements ($L\alpha_{1,2}$, $L\beta_1$ and $L\beta_2$) are located very conveniently 4) so that, e.g. the $L\beta_1$-lines of element (Z + 2) lie near to the $L\alpha_1$-lines of the Z th element. As a rule they can be used for the successive (one after another) analysis of these elements in a test mixture by the "line width" method.

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1) Photometrically.

2) The idea of this method was first put forward in 1937 [5]; its experimental testing and development however, as applied to the problems of optical and X-ray spectrographic analyses have only been carried out comparatively recently [6,7,3].

3) Since the ratio between S_{max}/S and I_{max}/I will be different for different points along the line contour.

4) Unless one takes into account several positions where the lines of the elements are superimposed, and which require great care on the part of the analyst.

In order to do this it is essential in the first instance to know Γ for the respective lines. For this determination a series of standard mixtures of the rare-earths were prepared, the composition of which was selected so that the intensity of the $L\beta_1$ line of one of the elements was equal to 0.5 of the intensity of a nearby $L\alpha_1$ line of another element. After this, the width of the $L\alpha_1$ line was measured at the height of the $L\beta_1$ line of another element contained in the mixture.

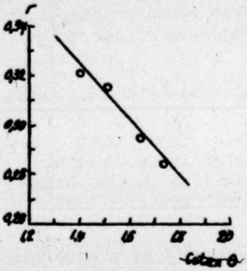

Fig. 1.

The values of Γ obtained in this way for various elements after averaging them on the basis of the results of several measurements were compared with each other. As was to be expected a straight line relation was found to exist between the half-width of the line of an element Γ and the cotangent of the reflection angle (Fig. 1). This relation enabled us to calculate the values of Γ for each of the 14 elements of the rare-earth group by relying on the experimentally determined values for those elements which we had at our disposal in a pure state.

A calibration curve was then constructed by means of which it was possible, in our case, to convert from the ratio of the line intensities of the elements compared as determined by the "line width" method to the ratio of their contents in a test mixture. This straight line, which is shown in Fig. 2, was constructed from the results of analyses of many standard mixtures of known composition, and, as was to be expected, remained unchanged for a given pair of compared elements, if the $L\alpha_1$ and $L\beta_1$ lines of each of the elements were chosen so that they lay close to one another. It is worth noting that the straight line in Fig. 2 is in good agreement with theory.

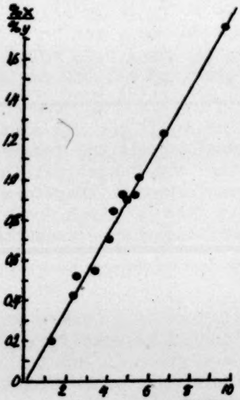

Fig. 2.

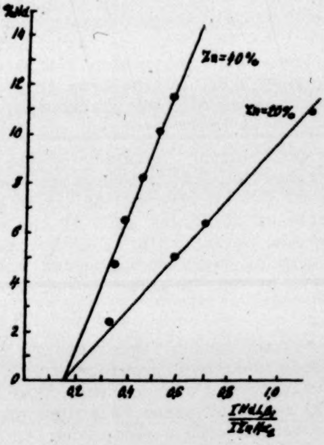

Fig. 3.

In order to recalculate the relative composition of a test sample on an absolute basis a known amount of a reference standard element was added. In the case under consideration it is convenient to use zinc[1] as the reference standard, the amount of the zinc can, generally speaking, be left unchanged in the mixtures, which differ in composition. Nevertheless, for convenience in carrying out analysis we usually introduced ca 20% of the reference standard when the test mixtures contained small amounts of the test elements, while for mixtures with higher percentage contents of the test elements we used 40% of the reference element.

In both cases the absolute content of a test element could be established on the basis of measurements of the width of the Zn $K\alpha_2$-line at the height of the $L\beta_1$-line for neodymium, and by using the straight lines shown in Fig. 3. The accuracy of the method was shown experimentally to be 4-6% of the actual content.

Quantitative X-ray Spectrographic Determination of Individual Elements of the Group

We shall consider next a more general case of analysis. For carrying out this analysis it is necessary to compare the intensities of lines which are located at large and unequal distances from each other against unequal backgrounds on the X-ray spectrograms. Under these conditions the "line width" method is not suitable.

Analysis can, however, be carried out simply and conveniently by a more general method which we have outlined previously [3], and which is based on the application of a transformation of the blackening function.

The latter function P is related to the blackening S by the equation $P = W + \underline{l}(S - W)$, where $S = \log \frac{i_0}{i}$, $W = \log \frac{i_0}{i} - 1$, while $\underline{l}$ is a constant which enables the characteristic curve of the emulsion to be "straightened". It has been shown that this is applicable both in the optical [9], and in the X-ray part of the spectrum [2,3]. In both cases $P = \gamma_p \log I - i_p$ holds for a wide range of line blackening, which practically overlaps all the region the analyst is interested in.

One outstanding feature[2] of the case under consideration of the use of the P-transformation for carrying out X-ray spectrographic analysis is the independence[3] of the transformation coefficients $\underline{l}$ and γ_p of the wave-length within the limits of the given part of the spectrum. The P-transformation therefore acquires the character of a universal transformation, the form of which for a chosen type of emulsion and under standard developing conditions is represented quite well by the formula

$$P = W - 1.13\ (S - W). \qquad (2)$$

The actual form of equation (2) is established experimentally by means of the methods described previously [3]. The method given in [1] is used for constructing blackening curves. The relations $P = P(S)$ are given in tabular form. By means of these relations it is possible to convert from blackening values measured with a photometer to P values, and vice-versa. Both the curves used in this work, viz. $S = S(I)$ and $P = P(I)$, are represented on the same scale in Fig. 4.

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[1] The choice of zinc was a convenient one from our point of view, but its use is not obligatory.

[2] In comparison with the general case put forward in [3].

[3] As our experiments showed.

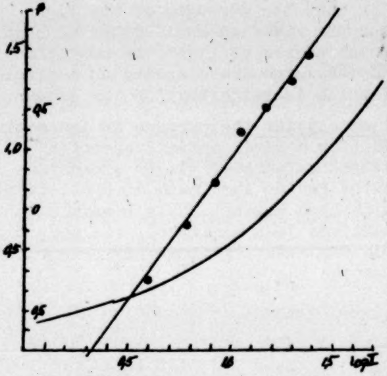

Fig. 4.

A knowledge of $P = P(I)$ enables one to determine the relative amounts of elements in the test mixture easily, independently of whether there are changes in the background values of the X-ray spectrogramm and of the mutual positions of the lines to be compared for the test elements. A series of calibration curves was therefore experimentally determined for this purpose for the elements under consideration, these curves related the values of $\frac{P_1' - P_1''}{\gamma_p}$ determined experimentally to the logarithms of the ratio of the concentrations of the elements compared in the test mixture. The values P_1' and P_1'' characterize the intensity of the lines compared after excluding the influence of the discontinuous background.

Some of these curves, which were obtained on comparing the analogous lines of elements with successively increasing atomic numbers, are shown in Fig. 5.

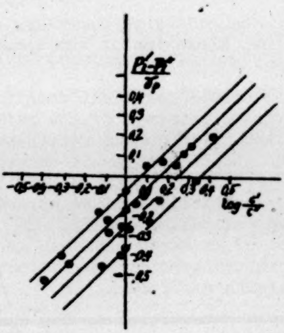

Fig. 5.

The straight line nearest to the origin was obtained by comparing the intensities of the $L\alpha_1$ lines of two elements following straight after each other; the second line by comparison of two elements separated by another element; the third line by comparison of two elements separated by two other elements etc. All of them, as was to be expected in agreement with [3], form a family of parallel straight lines which are separated from each other and make an angle of 45° with the abscissa.

The magnitude of the displacement of one line relative to the next is practically a constant and is equal to ca. 0.09.

Since in the given spectral interval the constant γ_p of the P-transformation, according to our measurements, does not undergo any significant changes, while $i_p' = i_p''$, the experimentally observed variations in the relation $\frac{p' - p''}{\gamma_p} = a + \log \frac{c'}{c''}$, on changing from one straight line to another (Fig. 5) could only be the result of a regular decrease in the sensitivity of the analysis for elements of the group considered in accordance with decreasing atomic number. On the other hand, the nearness of the excitation potentials of the test elements to each other and the complete standardization of excitation conditions of the X-ray spectrum which we try to attain during analysis, are not likely to lead to a similar conclusion; in any case it would be very unreliable. A more detailed treatment of this phenomenon would actually enable one to show that this is not an effect which is specific for the group of elements under consideration, but is a development of certain general geometrical relations which hold for the normal type of models of focussing X-ray spectrographs operating on the principle of internal reflection, and which has strangely escaped the attention of investigators hitherto[1]).

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[1]) As far as we could ascertain from published data.

In actual fact, an indispensable condition for the realization of X-ray elemental analysis by means of a quantitative comparison of the intensities of the X-ray lines of varying wave lengths, is that the strength of the light source remains strictly constant throughout the rotation angle interval used. In X-ray focussing spectrographs with a point source of light the condition is fulfilled automatically, if the source and its image are disposed on a circle touching the curved crystal, the radius of which is twice that of the latter.

For a number of reasons, however, but mainly for the purpose of increasing the overall power of the illumination used (for a given optimal specific loading of the X-ray tube), spectrographs with a focus of finite dimensions are used in practice, the focus being located inside the image circle. It is equivalent to an imaginary point source with high power. It is possible to show that under these conditions, the conditions just mentioned, viz. the uniformity of the power of the light source for every spectral line, is fulfilled only in the case where to a first approximation the value of

$d\omega = \frac{S\theta}{(r - a)^2}$ i.e. the value

$$\frac{S_\theta}{\left(\sin\theta - \frac{a}{R}\right)^2} \qquad (3)$$

remains a constant within the limits of the chosen interval of the reflection angle.

Here $d\omega$ is the element of the solid angle; R – the radius of curvature of the crystal; θ – the reflection angle; S – the optimal dimension of the focussing spot for a given reflection agnle and $r = R \sin\theta$.

What has been said above means that in order to create identical conditions for photographing the various lines disposed in a finite interval of the reflection angle, the size of the focussing spot of the X-ray tube of a Johann spectrograph should change according to a trigonometrical law, and should not remain constant as it does in a wide range of the appratus used in practice. Ignoring this fact will lead to the creation of an irregular scale of sensitivity for the apparatus, and to a decrease in the sensitivity with increasing reflection angles. The invariability of the magnitude of the focussing spot of an X-ray tube has as a consequence an actual decrease in the value of the active part of the reflecting crystal for large reflection angles in comparison with small ones.

In this connection, it follows from [3], that the intensities of the spectral lines for values of a/R which are small compared with $\sin\theta$ should decrease as $1/\sin^2\theta$. In the general case where a/R is relatively large, the law of decreasing line intensity with rotation angle is more complicated. Theoretical values of the magnitude of the effect, which can be derived by means of equation (3), appear to be of the same order as the experimentally observed values. Thus relying on a knowledge of the apparatus constants which are at our disposal, it should be possible to forecast the existence of a practically constant value for the displacement of one curve relative to another in Fig. 5 of ca. 0.06 as against the experimentally observed shift of ca. 0.09.

SUMMARY

1. The effectiveness of new X-ray spectrographic quantitative methods has been demonstrated in the case of a group of elements which it is difficult to analyze by other means.

2. It has been shown that for a given active part of the reflecting crystal in a Johann spectrograph in which the source of the X-rays is not located on the image circle and has finite dimensions, there is an optimal size for the focussing spot of the X-ray tube for a given reflection angle. This value to a first

approximation changes proportionally to $1/\sin^2 \theta$ and in general depends on the apparatus constants.

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A CARBONATE VARIANT FOR THE MASS SPECTROGRAPHIC ANALYSIS OF OXYGEN IN WATER

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The mass-spectrographic method of determining the isotopic composition of oxygen, which is, generally speaking, the most convenient and rapid method of isotopic analysis, loses its advantages in the direct analysis of water. The difficulties arise in this case as a result of the stability of the vacuum "water" background in the mass spectrometer and particularly as a result of the slowness of evacuation of the residual water vapor when exchanging the water samples being analyzed.

Another obstacle in the analysis of the rare O^{17} isotope is the capacity of water to give – on ionization of its molecules with electrons – secondary ions of the composition H_3O^+.

In order to accelerate the evacuation of water vapor from the ionization tube of the mass spectrometer, and consequently to speed up water analysis, it is possible to lower the adsorption of water by the apparatus walls by carrying out all the analyses in a heated spectrometer tube. An analogous method is used for mass-spectrographic analysis of easily liquefied hydrocarbons, in those cases where the construction of the apparatus enables one to work with a heated tube the method can be applied to the isotopic analysis of water.

It is possible, however, to get over these specific difficulties in the mass-spectrographic analysis of water by another method, viz., by converting the oxygen of the water into another molecular form which is more amenable to analysis. The success of such a method is determined by the simplicity of all the operations necessary for converting the oxygen of the water into the form of an "analytical gas" which can be analyzed readily by the mass spectrometer.

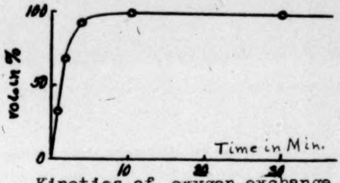
The best gas for isotopic oxygen analysis is CO_2 because of its ease of separation and purification, its ease of evacuation from a vacuum system, the purity of the vacuum background of the mass spectrometer in the region of the isotopic peak of CO_2 (masses 44-46), and finally because of the high ionizability of its molecules by electrons. In addition, the capacity of CO_2 to exchange oxygen with water enables one to introduce the oxygen from the test water into the CO_2.

Thus, isotopic analysis of water can be replaced by a much more convenient analysis of the oxygen of carbon dioxide, if one can guarantee beforehand complete exchange of oxygen between the water tested and the small amounts of CO_2 taken in definite amounts.

An analogous method for oxygen exchange in the system CO_2-H_2O has been used for the precision mass-spectrographic determination of heavy oxygen O^{18} in samples of sea water [1]. It is also obvious that this principle of the exchange and transfer of the oxygen under test into the "analytical" gas CO_2 is applicable for studying the composition of oxygen in other oxygen-containing compounds which are difficult to analyze, e.g., silicates, alumino-silicates, and oxides, if it is possible to find and work out the conditions necessary for realizing complete oxygen exchange between these compounds and CO_2.

Below we discuss the basis of a very convenient and simple carbonate variant for the isotopic analysis of water oxygen which does not require any additional apparatus; this is followed by a description of the actual technique employed.

This variant is based on the following results on the oxygen exchange between alkali carbonates and water.



Kinetics of oxygen exchange between K_2CO_3 and H_2O at 100°C.

According to experiments carried out by Mills and Urey [2], at room temperature, free CO_2 exchanges its oxygen for the oxygen of water at a moderate velocity, the time of half exchange $\tau = \approx 20$ minutes. Oxygen exchange between bicarbonates and water is somewhat slower, while the rate of exchange between normal carbonates and water is extremely low, the half exchange time $\tau = \approx 2$ days.

Increasing the temperature, however, has a considerable effect on the kinetics of oxygen exchange of dissolved carbonates; at 100° the oxygen of the water exchanges not only with bicarbonates CO_2 but with normal carbonates so rapidly that the respective constants can only be evaluated approximately; the half exchange time of K_2CO_3 with water $\tau = \approx 1$ minute, while exchange is practically complete after 10 minutes

The graph shown in the Fig. illustrates the curve we obtained for the kinetics of oxygen exchange between K_2CO_3 and water, during a study of the interaction of H_2O enriched with the O^{18} isotope with normal K_2CO_3. Similar experiments with sodium carbonate and CO_2 gave identical results; the exchange was so rapid that it was impossible to distinguish between carbonate and bicarbonate.

These experiments were carried out as follows. The carbonate solution was prepared first. 0.5 g of K_2CO_3 (normal composition) was dissolved in 10 ml of water enriched with O^{18} (1%). A test tube containing the solution was then immersed in a steam bath; after varying time intervals of 0, 1, 3, 10, 30 minutes, 1 ml aliquots were removed and rapidly (8 minutes) evaporated on a watch glass. The dry residue of carbonate was transferred on a boat to the inlet system of a mass-spectrometer, where the CO_2 was liberated from the carbonate into a vacuum by addition of pyrophosphoric acid. The extent of exchange was determined by the ratio of the isotopic peaks of CO_2 of masses 45 and 46, respectively.

The rapid assimilation of water oxygen by the dissolved carbonate at 100° enables one to evolve a very suitable form of the carbonate method of analyzing the isotopic oxygen composition of water. The following procedure can be recommended.

Into a small, dry test tube 50 mg of dry potassium carbonate is weighed out and 1 ml (or 0.5 ml) of the test water added to it. The test tube containing the dissolved potassium carbonate is stoppered and kept in a boiling water bath for 20 minutes so as to ensure complete exchange. The contents of the test tube are then poured out (no rinsing) on to a watch glass and rapidly evaporated to dryness on a sand bath. The dry carbonate containing the "water oxygen" is then analyzed in the mass spectrometer.

For comparative testing, exactly the same procedure must be adopted for the water taken as the standard, so that all the results can be related to the same standard. Comparative analyses increase the accuracy and simplify the calculation of results (see below). During analysis of a series, the exchange procedure should be carried out in one apparatus. The dry carbonate obtained after exchange can be kept in a desiccator (in order to avoid a reverse exchange) over solid NaOH.

The composition of the oxygen in the CO_2 evolved from the carbonate after exchange is not exactly the same as that of the oxygen in the test water. The ratio of O^{18}/O^{16} of this CO_2 and of the carbonate will differ from the O^{18}/O^{16} ratio of the water by a correction factor which depends on 1) the relative amounts of oxygen in the water and in the carbonate; and 2) on the constant of the isotope equilibrium in the system CO_3^{2-} - H_2O for oxygen at 100°. A knowledge of this correction, and consequently of the O^{18}/O^{16} of the original water can be calculated from the analytical results.

Let:

q and q' represent the percentage ratio O^{18}/O^{16} of the test water before and after exchange with K_2CO_3 respectively;

q_k and q_k represent the percentage ratio of O^{18}/O^{16} in K_2CO_3 before and after exchange.

m,n the relative number of oxygen atoms participating in this exchange in the carbonate and water respectively. It is then easy to show that

$$(q^{1}_{k} - q_k) \cdot m = (q - q') \cdot n. \qquad (1)$$

The ratio of q' to q'_k is the constant of the isotopic equilibrium in the system $H_2O - CO_3^{2-}$ at 100°. This ratio was calculated by Urey [3] and found to be equal to

$$K = q'/q'_k = 0.99 \qquad (2)$$

The ratio O^{18}/O^{16} of normal carbonate is ca. 0.2%; consequently $q_k = 0.2$. The value of O^{18}/O^{16} for water can then be calculated from the expression:

$$q = q'_k \cdot \left(0.99 + \frac{m}{n}\right) - 0.2 \cdot \frac{m}{n}. \qquad (2)$$

The value of q'_k for this equation was determined on the mass spectrometer as half of the percentage ratio of the 46 and 44 peaks of CO_2 evolved from the "exchanged" carbonate.

If the potassium carbonate and water used for the exchange are mixed in the ratio 5:100 or 10:100, then the value of m/n will be 0.02 or 0.04 respectively. Other ratios of m/n of course are permissible, within the limits of potassium carbonate solubility.

In comparative analyses one usually determines by how much the O^{18}/O^{16} of the test water exceeds that of a standard, i.e.

$$\Delta q = q - q_{stand}$$

is found.

From equation (2) it follows that this Δq of water is related to the respective increase $\Delta q'_k$ of the exchanged carbonates as follows:

$$\Delta q = \Delta q'_k \left(0.99 + \frac{m}{n}\right). \qquad (3)$$

For a 5% ratio of K_2CO_3 and H_2O, equation (3) has the form

$$\Delta q = \Delta q'_k \cdot 1.01$$

The method described is applicable to the analysis of oxygen in water enriched with heavy isotopes to give results with the usual accuracy of mass spectrographic methods. The applicability of the carbonate method for precision analysis of O^{18}/O^{16} of natural waters has not been studied.

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THE INDUSTRIAL IMPORTANCE OF ASCORBINOMETRY

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Commercial synthetic ascorbic acid is available in preparations of exceptional purity and can therefore be used for standardizing alkali solutions. In the case of ascorbic acid, however, its acidic properties are of secondary importance compared to its reducing properties, which are unusual for organic compounds and are the bases of its biological activity. Its reducing properties are the basis of methods used for determining "Vitamin C", since in the form of pure preparations it is easily titrated with iodine and can also be determined by the blue dye dichlorophenolindophenol, which reacts stoichiometrically with it. Analytical work relating to ascorbic acid has hitherto been confined to its determination, and only a few papers have been devoted to the use of its reducing properties for the determination of other materials. Without taking into account the preparation of certain colloids, and the determination of the noble metals with ascorbic acid, shortly before us, the Russian research workers Ptitsyn and Kozlov [1], used ascorbic acid for the potentiometric determination of trivalent iron. Fearing rapid decomposition of ascorbic acid in solution, they prepared fresh solutions every time, and during titration they added a known excess of ascorbic acid in the solid state and titrated the excess with 0.1 N iodine.

The authors [1] did not propose a method for working solutions of ascorbic acid which retain their reducing properties over long periods, nor considered the possibility of using ascorbic acid in other oxidation-reduction reactions. Because of its strong reducing properties, solutions of ascorbic acid are oxidized fairly rapidly, but the process only occurs rapidly, according to our work, in the presence of traces of metals which catalyze its oxidation. If, therefore, water which has been distilled in an all-glass apparatus free from any metals, particularly copper, is used for making the working solution, then its strength depreciates only to a very small extent even in air; when kept under CO_2 it retains its strength for weeks. On the basis of our work we can ascribe the decomposition of working solutions of ascorbic acid to two causes. Freshly prepared solutions initially lose their strength because of aerial oxidation catalyzed by copper ions. This decomposition amounts on an average to 0.3% per day when a solution which has been prepared from water distilled once in a glass apparatus is exposed to air. Subsequently, after a fairly long time, bacterial decomposition sets in, so that decomposition of a solution kept in an inert atmosphere sets in usually after 1-2 weeks. It became obvious that to prevent aerial oxidation it is necessary to complex copper ions or to convert them into insoluble precipitates. The suggested use of cyanides, thiocyanates and sulfides of the alkali metals is not a good one, because the presence of these salts severely limits the application of ascorbic acid solutions, and in any case these salts are not very effective. The proposal made very recently [2] that Trilon B (Complexone III) be used for the protection of ascorbic acid solutions does enable the catalytic activity of copper ions to be eliminated completely and thus increases the storage time of the solutions. Trilon B also hinders bacterial decomposition so that the solution can be stored for several months. It is best to keep solutions in a refrigerator at ca. +2°. A solution preserved by addition of Trilon B and stored in a refrigerator may be regarded as reasonably stable for a period of some months; we found that such a solution kept better than thiosulfate solutions.

Ascorbic acid solutions may be standardized by titration against 0.1 N iodine or against the iodine liberated on interacting potassium iodide with potassium iodate or biiodate. The results obtained are very accurate. Addition of starch at the end point is not recommended, since the starch slows down the reaction considerably. Standard ferric chloride can also be used for checking the standardization of ascorbic acid solutions.

It is advisable to prepare 0.01 N solutions of ascorbic acid freshly from 0.1 N solutions, although one keeps just as well as the other according to our work.

Bearing in mind the cheapness of ascorbic acid, it is reasonable to expect that it will take its place among other reducing agents.

The use of ascorbic acid solutions for the determination of a few oxidizable solutions was studied, and in some cases satisfactory results were obtained. Durint these preliminary tests the end point was chiefly determined potentiometrically. We have suggested the term "Ascorbinometry" for these methods [3]. We also established that ascorbic acid can be used in the molybdenum blue reaction for the determination of phosphates, arsenates, silicates and germanates. The oxidation of ascorbic acid depends on the nature of the oxidizing agent used.

Ascorbic acid is oxidized by oxidizing agents of average strength to dehydroascorbic acid; this process is fairly well defined and proceeds reasonably fast, so that for the majority of cases the fundamental reaction may be written:

$$C_6H_8O_6 = C_6H_6O_6 + 2H^+ + 2e.$$

It is often expedient to accelerate this reaction by means of catalysts or by heating the reaction mixture. Sometimes, particularly in hot solutions, the oxidation goes further until oxalic acid and l-threonic acid are formed. Strong oxidizing agents convert the latter into oxalic acid. If one bears in mind that hydrogen ions are formed during oxidation it is clear that the conditions for carrying out the individual methods must be carefully observed. During such investigations it is essential to establish the well defined course of the reaction, and to find the necessary conditions for carrying it out.

Determination of Trivalent Iron

From a practical point of view the determination of iron is of great interest, so that using the results of the Russian research workers mentioned already [1], we accordingly tried to develop a method for its determination. First of all it was necessary to elucidate the mechanism of the reaction and then to select the appropriate conditions for carrying it out. It was established that the reduction of trivalent iron ions, particularly in dilute solutions, proceeds slowly, and that the presence of thiocyanates slows down the reaction still more. In neutral solutions which are too hot, even dehydroascorbic acid can act as a reducing agent, as a result of which low results are obtained. Taking all these factors into consideration, titration should be carried out exactly as described below.

An almost neutral or neutralized solution of the trivalent iron salt is acidified with 5 ml of 2 N hydrochloric acid and titrated with 0.1 N ascorbic acid solution to the point where the yellow color of the solution disappears. The contents of the beaker are then heated to 60° and to the hot solution is added 1 ml of 0.5 N potassium or ammonium thiocyanate and the titration continued until the red color of the solution is not decolorized after standing for a few seconds. It is expedient to finish the titration within 5 minutes of starting to heat the solution and to try and get a final volume of ca. 100 ml. The accuracy of the method is 0.1%.

The determination, which is rapid and can be carried out without any special apparatus, gives very accurate results (see Table 1). The special advantage of the method is that it is applicable in the presence of nitrates, and in the presence of phosphates and fluorides; in this connection, it is the only method. Strong oxidizing agents such as nitrites naturally interfere, but their removal or the suppression of their influence is not usually difficult. The procedure described above can also be used for 0.01 N solutions.

TABLE 1

	mg Fe/ml			
In the form of Fe_2O_3 gravimetrically	Volumetric method			
	Ascorbic acid	Titanometrically	Zimmerman-Reinhart	Iodometrically
5.933	5.969	5.964	5.964	6.005
5.975	5.958	5.958	5.952	5.994
5.978	5.964	5.964	5.975	5.977
5.954	5.969	5.969	5.986	5.972
Mean 5.960	5.965	5.964	5.969	5.992
	Deviation of individual methods, in %			
-0.16	-0.08	-0.10	-0.02	+0.37

These advantages make the method a suitable one for industrial application. Recently the unusual increase in the practical application, particularly in production laboratories, of titanometric, chromometric, and vanadometric methods of determining trivalent iron has shown that these methods fulfill their purpose very well. It is the rapidity of reductometric methods for iron which is their chief advantage.

The conditions which necessitate keeping the working solutions under a protective gas and also titrating in an atmosphere of this gas, since basic reactions induce aerial oxidation, is a drawback of these methods as compared with oxidometric methods. It must be admitted, however, that the reductometric methods enumerated above have ousted oxidometric methods in modern laboratories because of the simplicity of preparation of test solutions, which in the majority of cases already contain the iron in a trivalent form. After removal of the nitric acid usually used for oxidation, the solution of trivalent iron can be titrated directly in the presence of a suitable indicator. When the ascorbinometric method is used there is no need to keep the solution under a protective gas and it is sufficient to check the standardization of the ascorbic acid solution once a day. Nitric acid does not interfere in the ascorbinometric determination of iron; the solution obtained, therefore, after dissolving the iron, can be titrated without evaporation of excess nitric acid. Titration in this manner is not sensitive to atmospheric oxygen so that there is no need to use a proctective gas. Ascorbinometric determinations of iron in comparison with other reductometric methods used in practice is less sensitive to interfering ions for an equal rate.

From what has been said above one may expect that the ascorbinometric determination of iron will be rapidly adopted in production laboratories and will take its place among more complicated reductometric methods. The fact that nitrates phosphates and fluorides in small amounts do not interfere with ascorbinometric determinations should contribute to making it a popular method. From this it follows that oxide, sulfide, and carbonate iron ores can be titrated directly after dissolving them in a mixture of nitric and sulfuric acids, while iron solutions after passing through the most diverse processes of separation can still be used for determination of the iron content after oxidation with nitric acid or hydrogen peroxide. These advantages are made most clearly evident in the determination of the iron content of bauxite, and in the usual analyses carried out in glass and ceramic laboratories. The method is eminently suitable for determination of iron in "luminous powders", the iron in these powders being present as the prosphates and fluorides. The iron can be determined directly by dissolving the sample in acid, oxidizing the iron with hydrogen peroxide and destroying the excess peroxide before titrating.

Titration can be accurately carried out by depolarization methods. A voltage of 0.14 V is applied to two platinum electrodes immersed in the solution to be titrated through a shunted micro-ammeter. When such a scheme is employed there is no need to use an indicator and the titration can be carried out in colored and completely opaque solutions It is convenient to use this variant, particularly in the presence of large amounts of Cr^{3+}, Ni^{2+} or Co^{2+}. The method is definitely a superior one for the determination of iron in metallic nickel, ferrochrome, and in chrome steels. A thermocouple placed in a gas burner flame can be used for measurements, no other special apparatus is required, so that this method cannot be ignored from the production laboratory point of view. The equivalence point can also be determined polarometrically(amperometrically) in this method.

Determination of Chlorates [5]

Ascorbic acid solutions are suitable for titrating iodine liberated from potassium iodide by oxidizing agents in acid media, and can practically completely replace sodium thiosulfate. This is true also in the case of chlorate ions; in this case however we have managed to find a direct titration method. The obvious advantage of this method is that it is a direct one. After a consideration of the general methods known for the determination of chlorates we came to the conclusion that chlorate ions, which are particularly stable because of the symmetry of their electronic system, are reduced only in strong acid media, and only in auto-catalytic or catalytic processes. We therefore had first of all to establish whether ascorbic acid can be used in strong acid solution, and then find a suitable catalyst. It was established that under conditions where the reduction of chlorates is speeded up, the ascorbic acid which is in excess during titration does not decompose appreciably, even in 4N sulfuric acid at 60°. The catalysts which are normally used in oxidation-reduction titration processes proved to be useless for our purpose. Selenious acid, however, proved a suitable indicator; at the end point in this case, elemental selenium is released. In a series of careful experiments it was established that excess chlorates are not reduced under the optimal conditions for determination of dehydroascorbic acid. During a study of the effect of other ions it was found that reproducibility of results was better in the presence of Mn^{2+} ions, since in this case a local excess of ascorbic acid does not lead to a premature separation of selenium. Taking into account all these factors, the following technique may be adopted.

To the solutions containing chlorate are added 8 N sulfuric acid and distilled water in such amounts that at the end of titration the sulfuric acid concentration is 4 N while the final volume is 100 ml. The solution is then heated to 60° and 10 ml of 0.1 M selenious acid added together with 5 ml of 20% $MnSO_4$ solution. 0.1 N ascorbic acid is added from a buret with vigorous stirring until 1 ml has been added, when the solution is again heated to 60° and titration is continued till a definite orange color appears. At this point one should wait not less than 10 seconds after the addition of each drop.

TABLE 2

Test material	Active chlorine content, %	0.1 N ascorbic acid used (ml)	Found	
			$NaClO_3$ (g/liter)	$Ca(ClO_3)$ (g/kg)
100 ml freshly prepared solution of NaOCl.........	0.79	0.15	0.0027	
100 ml freshly prepared solution of NaOCl + 5 ml 0.1 N $NaClO_3$ solution.....	0.79	5.17	0.0917	
100 ml freshly prepared solution of NaOCl + 10 ml 0.1 N $NaClO_3$ solution.....	0.79	10.20	0.1809	
100 ml freshly prepared solution of NaOCl + 20 ml 0.1 N $NaClO_3$ solution.....	0.79	20.12	0.3569	
100 ml solution of NaOCl after standing 14 days....	5.92	2.86	0.0507	
10 ml of commercial hypochlorite solution.........	3.63	33.50	5.943	
5 ml of NaOCl solution after standing for a few months..................	5.38	45.55	16.163	
1.00 g of chloride of lime	27.80	17.80		36.64

This method does away with the use of expensive iodine compounds, but is not inferior to other methods of determining chlorate with respect to accuracy. This method can be applied to the determination of chlorates in hypochlorites. It was found that on boiling with H_2O_2 in alkali solutions, hypochlorites are broken down without formation of chlorate, while the chlorate can be determined in the acidified solution by the method described above; the results are given in Table 2. This method is applicable to the determination of chlorates in bleaching powder and in the alkali metal hypochlorites, and also in the mother liquors resulting from the electrolysis of alkali metal chlorides.

Determination of Iodates

We have also found a direct method for determining iodates [6], without using potassium iodide. It was established that on titrating solutions of potassium iodate in acid media without addition of potassium iodide the iodide ions formed on reduction react with excess iodate ions to give iodine, which temporarily settles out in the solid form and which only reacts with ascorbic acid after complete reduction of the iodates; the end point is determined by the complete disappearance of elemental iodine. We succeeded in increasing the accuracy of the method further on the basis of the fact that the iodide ions formed as intermediates can by complexed with $HgCl_2$. As a result, the reduction of iodate can proceed in one stage without a transitional separation of iodine. Determination of the end point is based on the fact that excess ascorbic acid reduces mercuric chloride to mercurous chloride. Mercurous chloride, however, only precipitates at the end of the titration when selenious acid is used as a catalyst. Determinations were made as follows:

The neutral or neutralized solution of iodate is acidified with 10 ml 0.1 N HCl, and then 10 ml of 0.1 N selenious acid and 15 ml of a saturated solution of mercuric chloride added, water being then added until the final volume is ca. 100 ml. The solution thus prepared is titrated with 0.1 N ascorbic acid, titration being slowed down toward the end point, and the slightest turbidity is taken as the end point.

The method was proved to be very accurate even when using 0.01 N solutions, although a small indicator error creeps in thereby. The method is capable of wide application, because by its application iodides and even free iodine can be determined, if the solution is first treated with bromine water and the iodides converted into iodates, the excess bromine being removed with formaldehyde. This "multiplication" method among other things enables one to repeat a determination, the iodide present in the already titrated solution being again oxidized to iodate (see Table 3).

Table 3

0.1 N KI (ml)	0.1 N ascorbic acid solution used in ml		
	First	Second	Third
20.00	19.97	19.95	20.08
	19.97	20.06	20.06
	19.99	19.82	20.10
	19.98	20.06	20.04

Table 4

Sample No. 1		Sample No. 2	
mg I_2/ml	mg KI/ml	mg I_2/ml	mg KI/ml
66.0	20.9	66.0	24.8
66.0	21.0	66.1	25.0
66.2	20.6	66.1	25.2
66.2	21.0	66.2	25.0

Bromine dissolves the calomel, while it converts the dehydroascorbic acid into an oxidation product which does not interfere. This cheap method is suitable for the determination of iodine content in iodine compounds and also in mineral waters. The advantages of this method are clearly demonstrated in the analysis of tinctures of iodine (see Table 4), in this case one can first of all determine free iodine after dilution with alcohol and then after removal of alcohol and oxidation with bromine the total iodine content can be determined, all with one working solution - ascorbic acid. Moreover, this method is accurate and more rapid than the methods of determination used in pharmaceutical chemistry.

Determination of Bromates

The determination of bromates [7], with ascorbic acid is carried out in a similar way to that for iodates. This method is only of importance for the analysis of alkali metal bromates.

Ascorbinometric Determination of Quinquevalent Vanadium

We have hitherto developed two methods; one a rapid method which is reasonably accurate for production analysis, and the other a more accurate one which has, however, a more restricted use. The first method is based on direct titration of quinquevalent vanadium in acid media with ascorbic acid to give quadrivalent vanadium. For the detection of the end point two new oxidation-reduction indicators - p-methoxy and p-ethoxy diphenylamine are used. Quinquevalent vanadium oxidizes both indicators to a dark violet color, while ascorbic acid in reducing them also decolorizes them. The color change is reversible, but over a prolonged time quinquevalent vanadium itself uses up the indicator, i.e. an irreversible oxidation takes place to an insignificant extent. This fact, however, does not affect the practical application of the indicators. The accuracy of titration is of the order of a few percent; this is a result of the fact that dehydroascorbic acid reduces quinquevalent vanadium, though slowly, while the interaction between ascorbic acid and quinquevalent vanadium is also slow. When, however, the titration is carried out rapidly, and this can be done easily after practice, the deviation of the results becomes very small. This method is recommended particularly for rapid technical analyses, e.g. for the determination of vanadium in vanadium or clay factories. An aliquot of the vanadium solution is dissolved in a small volume of sulfuric acid and the vanadium oxidized to the quinquevalent stage with potassium permanganate, excess of which is destroyed with oxalic acid; the quinquevalent vanadium is then titrated with 0.1 N ascorbic acid in the presence of p-ethoxy or p-methoxy diphenylamine. The determination can be repeated if the quadrivalent vanadium is first oxidized back again to the quinquevalent stage.

The more accurate method consists in adding excess ferrous sulfate to the acidified test solution of quinquevalent vanadium, through a reduction tube filled with metallic cadmium, whereby an equivalent amount of trivalent iron is formed, which is equivalent to the quinquevalent vanadium present; this trivalent iron is then titrated with 0.1 N ascorbic acid, using thiocyanate as indicator. Consequently instead of the highly oxidized quinquevalent vanadium, a system with a considerably lower oxidation-reduction potential is titrated; as a result the determination is more accurate because the dehydroascorbic acid does not react under these conditions.

Ascorbinometric Determination of Quadrivalent Cerium in the presence of ferroin as indicator has been carried out. The use of ascorbic acid is being extended for the determination of other oxidizing agents, and we hope that it will find even wider application.

Among further possible applications of ascorbic acid we may mention the determination of oxygen dissolved in water and the oxygen content of various gas mixtures. The importance and industrial significance of these determinations are obvious. In this connection a reduction pipet which we have designed may be useful. A solution of ferrous sulfate which does not contain any trivalent iron is added to the test water through the reduction pipet filled with powdered metallic cadmium, so as to form a separate layer underneath the water; the solution of ferrous salt is then vigorously shaken in a hermetically sealed flask, whereby the $Fe(OH)_2$ reacts to form $Fe(OH)_3$ in an amount equivalent to that of the dissolved oxygen. The hydroxide is allowed to settle and hydrochloric acid is carefully added to dissolve the precipitate; the solution of ferric chloride is then titrated with ascorbic acid. When only a small amount of dissolved oxygen is involved, the trivalent iron is determined colorimetrically with ammonium thiocyanate. Our results indicate that the method is fully equivalent to Winkler's method. Even the Winkler method can be converted into an ascorbinometric method if a strongly acidified solution of ferrous sulfate is added to the precipitated manganous hydroxide through the reduction pipet, and the trivalent iron titrated with ascorbic acid. Oxygen may be determined in gas mixtures on the basis of this method. Ferrous sulfate and sodium hydroxide are added in succession to a gas buret of known volume; after oxidation and acidification the trivalent iron ions, which are formed in an amount equal to the oxygen content are titrated. This method is of considerable importance for the determination of oxygen in boiler water and tap water and also in gas analysis. One of our future problems is the micro-determination of oxygen, in which the oxygen reacts directly with ascorbic acid in the presence of a catalyst.

Other Applications of Ascorbic Acid

Among other possible analytical applications of ascorbic acid we may mention micro-colorimetric determination of phosphates, germanates [8], silicates, and arsenates. Methods have already been worked out in full for the first two. The method is suitable for the quantitative determination of traces of phosphates. Mention may be made of the determination of phosphine in acetylene, in which only a very small amount of gas is necessary for analysis. The method for germanate is of interest from the point of view of ore prospecting. It is pertinent to mention here the recent successes of Soviet research workers on ultra-violet titration [9], in which ascorbic acid can be titrated with a solution of ferric chloride, the end point being determined by the capacity of the ferric chloride solution to absorb the ultra-violet, while the ascorbic acid does not.

What has been said above clearly shows that a number of analytical problems which are of industrial importance have already been solved. One can assume that further research into the possibilities of the method will facilitate the analyst's work, and make it simpler and more reliable.

One must mention that nearly all my colleagues at the Department of General Chemistry of the Budapest Polytechnical Institute participated in the development of "Ascorbinometry", in particular I refer to Dr. E. Bodor and B. I.Papp, who did most of the work.

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A SPECIFIC METHOD FOR THE DETERMINATION OF CARBONYL GROUPS IN HYDROXYCELLULOSES

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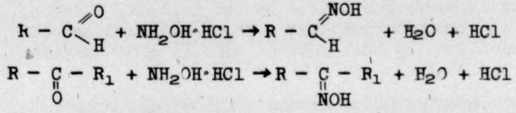
We have shown previously [1], that apart from carboxyl and aldehyde groups there are also keto groups in certain hydroxycelluloses. In order to determine total carbonyl groups in hydroxycellulose a method has been suggested which is based on condensation with hydroxylamine hydrochloride [2]; the method was first used for the quantitative determination of carbonyl groups by Petrenko-Kritchenko in 1901 [3].

The method is based on the following reactions:



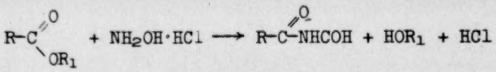
$$R-C\begin{matrix}\diagup\!\!\!\diagup O\\ \diagdown H\end{matrix} + NH_2OH\cdot HCl \rightarrow R-C\begin{matrix}\diagup\!\!\!\diagup NOH\\ \diagdown H\end{matrix} + H_2O + HCl$$

$$R-\underset{\underset{O}{\|}}{C}-R_1 + NH_2OH\cdot HCl \rightarrow R-\underset{\underset{NOH}{\|}}{C}-R_1 + H_2O + HCl$$

Oxime formation occurs in weak acid media at a pH of 5-6. The carbonyl groups are estimated from the amount of hydrochloric acid released. There are certain characteristic features of this reaction when applied to carbohydrates. It has been established that certain sugars react rapidly with hydroxylamine – 1-1.5 hours (maltose, galactose, arabinose), while others react slowly – 10-18 hours, (glucose, fructose, cellobiose). The percentage of carbonyl groups found experimentally in the sugars is 95-103% of theory. When working with hydroxycellulose the reactions occur in a heterogenous medium. It has been found that with hydroxycelluloses obtained by oxidation with CrO_3 and HIO_4 the reaction proceeds relatively quickly – 1.5-2 hours. The presence of carboxyl groups interferes with the determination, since under the experimental conditions (pH 5-6) the carboxyl groups can also react with hydroxylamine to form salts. Carboxyl groups should, accordingly be neutralized first of all by treating the test material with a calcium acetate solution. The accuracy of the method has only been checked on hydroxycelluloses prepared by periodate oxidation, and containing large amounts of aldehyde groups and small amounts of carboxyl groups; it was found that the reproducibility is of the order of ±1%.

We tried the method for the determination of keto groups in hydroxycelluloses. In addition to determining total carbonyl groups by the hydroxylamine method, we also determined aldehyde groups iodometrically [4]. The amount of keto groups was determined by difference between total carbonyl and aldehyde groups.

Having tried the hydroxylamine method, we soon found that it possesses a number of drawbacks, the main one being its lack of specificity. We have previously established that in hydroxycelluloses obtained by oxidation with hypochlorites in acid media, or those subjected to prolonged de-ashing with acids, lactone bonds are formed as a result of interaction between neighboring carboxyl and hydroxyl groups. Lactone groups, just like complex ester groups, can react with hydroxylamine to form hydroxamic acids.



$$R{-}C(=O)OR_1 + NH_2OH\cdot HCl \longrightarrow R{-}C(=O){-}NHCOH + HOR_1 + HCl$$

This reaction, according to published data, can occur in weakly alkali, neutral, or weakly acid media. We have demonstrated the formation of hydroxamic acids by condensation of hydroxycelluloses, prepared by hypochlorite oxidation with $NH_2OH\cdot HCl$, by qualitative tests for hydroxamic acids [5]. After interaction with hydroxylamine in a weakly alkali medium, the hydroxycellulose acquires a rose color on testing with $FeCl_3$ in a weakly acid solution as the result of complex formation between iron and the hydroxamic acids. As a result of this secondary reaction, results of titrations of HCl liberated are higher than the true content of carbonyl groups in the hydroxycelluloses. In order to avoid this it is essential, therefore, to increase the specificity of the method, and this was achieved by lowering the pH during condensation from 5-6 to 3-4. In a more acid medium only the carbonyl groups react; the lactone groups do not condense. Since at such a low pH a partial hydrolysis of the oxime is possible, the aqueous medium was replaced by an alcoholic one. The completeness of condensation of the carbonyl groups at a pH of 3-4 was checked by comparing the results of determination of aldehyde groups in hydroxycellulose by two methods, first, by condensation with hydroxylamine in alcoholic media at a pH of 3-4, and second, iodometrically. The results obtained by both methods were in good agreement; e.g. the following results were obtained:

1) by the modified hydroxylamine method - 0.109% CHO groups

2) iodometrically - 0.115% CHO groups.

This confirms that the cellulose carbonyl groups react quantitatively with hydroxylamine at a pH of 3-4.

In order to obtain a more convincing proof of the participation of lactone groups in the reaction with hydroxylamine during the determination of carbonyl groups, the following test was made. Hydroxycellulose was worked up with a 1% solution of sodium carbonate at 40° for 30 minutes in order to destroy the lactone bonds. After washing with water and drying in air, determinations of the carbonyl groups in an aqueous medium at pH 5-6 and also by the new method in an alcoholic medium at pH 3-4 gave similar results. Use of the method involving an aqueous medium at pH 5-6 gave a value of 0.18% keto groups, while the new method in which an alcoholic medium at pH 3-4 is used gave a value of 0.17%. Both methods, therefore, gave the same results in the absence of lactone groups. In practice, however, we cannot recommend a method in which the lactone groups are destroyed beforehand by an alkali treatment, because, as is known from previous work, even a short time in the alkali medium can lead to partial solution of and change in the hydroxycellulose.

Another drawback of the hydroxylamine method of determining carbonyl groups in hydroxycellulose is the impossibility of standardizing the results obtained by titration of liberated HCl, against determinations of the nitrogen combined during condensation.

Using the hydroxylamine method, we calculated the total aldehyde + keto groups from the titration results. The values obtained were checked against the nitrogen content of the oximes formed. In order to do this the hydroxycellulose which has reacted to give the oxime was carefully washed with water and dried, and the oxime nitrogen determined by a micro Kjeldhal. The large number of determinations which we made showed that the nitrogen content was always lower than that calculated from the carbonyl groups as determined by titration. On an average, the ratio of carbonyl groups according to nitrogen determinations to carbonyl groups determined by titration amounted to 60-65% (Table 1).

We checked the accuracy of the nitrogen determinations in the cellulose-oximes by the Kjeldhal method by comparing the results with those of nitrogen determinations carried out by the Dumas method; good agreement was obtained.

Table 1

Deviation between content of carbonyl groups as determined volumetrically with $NH_2OH \cdot HCl$ in aqueous media, and as determined from the nitrogen content of the oximes formed (aqueous media pH 5-6)

No. of test	Carbonyl groups found		Ratio of carbonyl groups found by the nitrogen to that found by titration
	By titration (%)	By nitrogen (%)	
1	0.33	0.23	
	0.33	0.23	69
2	0.34	0.28	
	0.36	0.30	82
3	0.54	0.34	
	0.53	0.32	62
4	0.44	0.30	
	0.46	0.32	68
5	0.30	0.17	
	0.28	0.18	62

Table 2

Determination of carbonyl groups in hydroxycelluloses at a pH of 5-6 in alcohol media

No. of preparation	Carbonyl groups found		Ratio of carbonyl groups by nitrogen and by titration in %
	By titration (%)	By nitrogen (%)	
2	0.35	0.34	
	0.37	0.35	94
3	0.55	0.45	
	0.57	0.45	82
4	0.46	0.42	
	0.44	0.43	95
5	0.30	0.27	
	0.25	0.26	93

The disagreement between the amount of carbonyl groups as determined by titration and as determined by the nitrogen content may be the result of instability on the part of the oximes or of the nitrogen-containing groups in the hydroxycellulose in aqueous media, or the solubility of low molecular weight oxidation fractions of cellulose in water. A survey of the large number of experiments carried out under different conditions leads one to the conclusion that the reason for the disagreement in the analytical results is the instability of the hydroxamic derivative of the hydroxycellulose. The following facts seem to favor this hypothesis. Carbonyl groups and nitrogen were determined, respectively, in hydroxycellulose which was known to contain no lactone bonds after preliminary treatment with dilute alkali. In this hydroxycellulose, the percentage of carbonyl groups as determined by the titration method (0.18%) was close to that found from nitrogen determinations (0.20%). In the absence of lactone groups, therefore, both methods give results in good agreement.

It was shown that when condensation with hydroxylamine was carried out in an alcohol medium at a pH of 5-6 (Table 2), the titration results approximated to nitrogen determination results. Under these conditions both the carbonyl as well as some of the lactone groups react, but no nitrogen of the hydroxycellulose oxime is lost. As a result, the hydroxamic derivatives of the hydroxycellulose which are broken down during water washing are stable in alcoholic media.

Results of condensation in alcoholic media at lower pH's also practically coincide, but the absolute values are lower than in the preceding case since in this case only carbonyl groups undergo condensation (Table 3).

When condensation is carried out at a pH of 3-4 there is no need for a preliminary neutralization of the carboxyl groups of the hydroxycellulose by treating with calcium acetate, since the extent of the dissociation of the COOH- groups at this pH in an alcoholic medium is insignificant. From work on the determination of carbonyl groups in low molecular weight compounds, it is known that in an alcoholic medium at a pH of 2.5 the presence of organic acids does not affect the accuracy of the determination [6]. We confirmed this in the case of hydroxycellulose, by carrying out parallel experiments on the determination of carbonyl groups in the same preparation with and without neutralization of the COOH groups (Table 4).

Results of comparative determinations of carbonyl groups by two methods the hydroxylamine method of Gladding and the specific method which we have put forward are given in Table 5. Values for the carbonyl group content as determined from oxime nitrogen are also given in the Table.

Table 3

Determination of carbonyl groups in hydroxycelluloses at a pH of 3-4 in alcoholic media

No. of preparation	Carbonyl groups found		Ratio of carbonyl groups by nitrogen and by titration
	By titration (%)	By nitrogen (%)	
1	0.26	0.23	91
	0.25	0.23	
2	0.31	0.26	86
	0.30	0.27	
3	0.29	0.29	100
	0.30	0.29	
4	0.29	0.25	96
	0.26	0.26	
5	0.20	0.20	100
	9.21	0.20	

Table 4

Determination of carbonyl groups in alcohol media at different pH values without preliminary neutralization of the hydroxycellulose, and after neutralization

No. of preparation	Carbonyl groups found, pH 3-4, alcoholic media		Carbonyl groups found pH 5-6 alcoholic media	
	Without neutralization	After neutralization	Without neutralization	After neutralization
1	0.26	0.23	0.51	0.33
2	0.30	0.28	0.68	0.36

The results given in Table 5 show that the values found for the carbonyl groups by titration according to our specific method are less than the values found by Gladding's method as a result of the exclusion of reactions involving lactone groups. At the same time they are very near to the values found via nitrogen determinations.

Thus, an experimental check on Gladding s method has shown that this method gives results for the carbonyl groups which are too high in the case of hydroxycelluloses produced by hypochlorite oxidation; it thereby gives values which are too high for the keto-groups when the keto groups are determined from the difference between total percentage of carbonyl groups and percentage of aldehyde groups. All hydroxycelluloses containing lactone bonds will give this error. The true percentage of carbonyl groups in the presence of lactone groups can be obtained if the analysis is carried out under the conditions described in the present article.

TABLE 5

Determination of carbonyl groups in hydroxycelluloses by various methods

Preparation.	pH	Carbonyl groups found by titration (%)		Carbonyl groups found by nitrogen (%)	
		Gladding's method	Our method	Gladdings method	Our method
Oxidized with NaClO	4.6	0.33	0.25	0.23	0.23
Ditto	7	0.35	0.27	0.29	0.26
Ditto	4.0	0.53	0.29	0.33	0.29
Ditto	6.5	0.44	0.28	0.31	0.26
Ditto	9	0.29	0.20	0.18	0.20

Description of Analytical Procedure

Reagent solution is prepared as follows: 5 g of hydroxylamine hydrochloride is dissolved in 240 ml of 96% ethyl alcohol + 5 ml of water + 6 ml of a 0.2% alcoholic solution of bromophenol blue. To the yellow solution obtained is added 0.2 N NaOH dropwise until a color which differs according to which way it is viewed is developed (green in transmitted light and red in reflected light). The pH of the reagent should be within the limits 3.2 - 3.4, and this is checked potentiometrically. The reagent solution is freshly prepared before each determination. 2-3 g of hydroxycellulose is added to 60 ml of reagent and allowed to stand at room temperature for 2 hours. After the 2 hours the hydroxycellulose is filtered off and 50 ml of filtrate taken for titration. The hydrochloric acid liberated on condensations is titrated with 0.1 N NaOH till the two-color solution is obtained as before. Titration is carried out more accurately potentiometrically to a pH of 3.2. From the amount of 0.1 N NaOH used for titration, the percentage of carbonyl groups in the aliquot of hydroxycellulose taken can then be calculated by means of the formula:

$$x = \frac{a \cdot 0.0028 \cdot 1.2 \cdot 100}{\text{weight taken in g}}$$

where a is the amount of 0.1 N NaOH used for titration, in ml.

SUMMARY

1. The method described in the literature for the determination of carbonyl groups in hydroxycellulose, and which is based on condensation of the groups with hydroxylamine hydrochloride, gives results which are too high, as a result of the presence of lactone groups in the hydroxycellulose, which form hydroxamic acids with $NH_2OH \cdot HCl$.

2. Condensation of lactone groups with $NH_2OH \cdot HCl$ can be excluded by lowering the pH from 5-6 to 3-4 and simultaneously changing over from an aqueous to an alcoholic medium. Under these conditions only the carbonyl groups react.

3. The use of a more acid alcoholic medium decreases the degree of dissociation of the carboxyl groups in hydroxycellulose to such an extent that neutralization with calcium acetate before a determination is unnecessary. Neutralization of carboxyl

groups is essential only when there is a high percentage of COOH groups, e.g., in cellulose oxidized with nitrogen peroxide.

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THE PERSULFATE-COBALT METHOD OF DETERMINING MANGANESE AND CHROMIUM IN STEELS AND CASTS IN THE SAME ALIQUOT

L.M. Kulberg, L. A. Molot, and L. F. Grigoreva

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Recently several attempts have been made to work out a persulfate method for the determination of manganese in ferrous and non-ferrous metals in which silver is replaced by other, less expensive catalysts. Thus, mercuric nitrate has been suggested as a catalyst (cobalt and chromium interfere in this determination). Kuznetsov and Budanova [1], have proposed cobalt sulfate as a catalyst, either on its own or with nickel sulfate or cupric sulfate. This last method is of considerable interest, particularly for factory laboratories, and in this connection we have subjected their method to a detailed check under the conditions of a factory laboratory for a series of determinations.1)

As a result of these tests it was established that:

1. Kuznetsov and Budanova's method is applicable to the determination of manganese in all the alloys tested: low and high alloy steels, casts, magnesium and aluminum alloys.
2. Of the three catalysts proposed by these authors the best results are given by the cobalt-nickel and cobalt-copper ones. The cobalt catalysts give somewhat lower results (of the order of 0.02 - 0.03%), which is obviously determined by some difficulty in determining the end point or by incomplete oxidation of the manganese.
3. There is no difference in the time taken to carry out analysis with silver as a catalyst or with the substitutes as catalysts.
4. For the analysis of simple or low alloy steels the amount of sample taken is 0.5 g while for casts the amount required is 0.2 g. Half the amount of persulfate stipulated in the recommended method is then sufficient for oxidation of the manganese in routine analysis.
5. Simple and low alloy steels can be dissolved in sulfuric acid (1:3) and they can be subsequently oxidized with a few drops of concentrated nitric acid.
6. Deviations from Kuznetsov and Budanova's method in the use of excess acid for dissolving the aliquot leads to low results. Oxidation of manganese by persulfate solution should only be carried out during boiling; addition of oxidizing agent to a solution which is not boiling leads to low results.
7. The undoubted advantages of the persulfate-cobalt method for determining manganese as compared with the persulfate-silver method recommend its wide use in factory and research laboratories.

Results are given below of the analysis of a number of metals by the persulfate-cobalt method (cobalt-nickel or cobalt-copper catalysts).

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1) Assistant A. G. Kovaleva also participated in checking the method.

Table 1

Results of the determination of manganese in several metal samples by the persulfate-cobalt and persulfate-silver methods

No.	No. of sample	Manganese % by $AgNO_3$ method	Manganese by the persulfate-cobalt method
1	Normal 6-a	1.18	1.18; 1.16; 1.18; 1.17; 1.18
2	Normal 286	0.40	0.40; 0.40; 0.40; 0.40
3	Normal 124	0.57	0.57; 0.56
4	Normal 83	0.61	0.60
5	Cast-alloy	0.83	0.83; 0.83; 0.82; 0.80; 0.81; 0.81; 0.82; 0.83 1)
6	Simple steel	0.59	0.59; 0.61; 0.60; 0.60; 0.61; 0.59 0.59 2)
7	Cast 1331	0.74	0.73; 0.73
8	Cast 1332	0.71	0.71; 0.71
9	Steel 20-X	0.66	0.66; 0.66
10	Steel 20-X	0.63	0.63; 0.63
11	Forged piece 1404 I	0.63	0.61
12	Forged piece 1404 II	0.69	0.68
13	Forged piece 1398 I	0.62	0.61
14	Forged piece 1398 II	0.60	0.58
15	Forged piece 1370	0.68	0.68; 0.68
16	Forged piece 1412	0.62	0.60
17	Duralumin S.O. 69	0.69	0.70; 0.71
18	Magnesium Alloy	0.25	0.23; 0.24

During a study of the persulfate-cobalt method of determining maganese it was found that this method is also applicable to the determination of chromium immediately after determining the manganese.

Simultaneous determination of manganese and chromium on one aliquot of cast iron or steel doubles the speed of analysis and leads to a considerable saving in reagents. Such a method is particularly useful in express analysis or during smelting. 3)

This method consists essentially of the oxidation of chromium with a persulfate solution in the presence of a cobalt-copper or cobalt-nickel catalyst to bichromate; after the manganese has been determined by the arsenite method, the

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1) The other nine results are the same, and equal to 0.83%.

2) The other six results which are not enumerated are all 0.59%.

3) The simultaneous determination of chromium and manganese by the persulfate silver method on one aliquot has already been adopted in the chemical laboratory of the "Hammer and Sickle" factory at the instigation of Chemical Engineers Simakina and Grigoreva.

bichromate is titrated with Mohr's salt in the presence of phenylanthranilic acid.

This method is applicable to steels containing up to 1.5% chromium. When the method described below was used, the results given in Table 2 were obtained.

These results show that the deviation between the method accepted at present and the method which we propose is within the limits of experimental error.

Table 2

Results of comparative determinations of chromium by the persulfate-silver and by the method suggested

No. in order	Sample Designation	Chromium % found by persulfate-silver method	Chromium % found by persulfate-cobalt method
1	Forged piece 50	0.94	0.92; 0.92
2	Forged piece 50-a	0.96	0.94; 0.96
3	Normal	1.56	1.53; 1.56
4	Forged piece 1382 I	0.95	0.94
5	Forged piece 1382 II	0.95	0.94
6	Forged piece 1404 I	0.73	0.76
7	Forged piece 1404 II	0.85	0.87
8	Forged piece 1398 I	0.85	0.84
9	Forged piece 1398 II	0.87	0.88
10	Forged piece 1379 I	1.04	1.06
11	Forged piece 1412	0.94	0.96
12	Forged piece 1379 II	1.00	1.00

Experimental Procedure. 0.5 g of steel or 0.2 g of cast is dissolved in 25 ml sulfuric acid (1.3), and oxidized with a few drops of concentrated nitric acid. The solution is heated until all the nitrogen oxides have been removed, when it is diluted with 150 ml of hot water, and 10 ml of the Kuznetsov-Budanova solution of cobalt-nickel or cobalt-copper catalyst immediately added (the cobalt-nickel catalyst is an aqueous solution containing 0.5% $CoSO_4 \cdot 7H_2O$ and 1.5% $NiSO_4 \cdot 7H_2O$; while the cobalt-copper catalyst is an aqueous solution containing 0.5% $CoSO_4 \cdot 7H_2O$ and 2% $CuSO_4 \cdot 5H_2O$). The mixture is brought to the boil. 15-20 ml 20% ammonium persulfate solution is carefully added to the boiling solution and the whole brought up to the boil again and boiled for 2-3 minutes. The solution is kept on a hot plate until the ammonium persulfate ceases to decompose when it is cooled in running water. 10 ml of sulfuric acid (1:3) is added to the solution which has been cooled to room temperature and the solution titrated with a solution of sodium arsenite1) to a change from violet to yellow (manganese determination). 4-5 drops of a phenylanthranilic acid solution is immediately added to the yellow solution (0.2 g of the acid is dissolved in 100 ml of boiling water containing 0.2 g sodium carbonate). After 1 minute the solution which is now a violet-wine color is titrated with a solution of Mohr's salt to a green end point (chromium determination).

The time taken for a chromium determination after titration of permanganate is not more than 3 minutes.

The method described in the present article is being used in a number of metallurgical and metal working factories.

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1) In this case an arsenite nitrite mixture cannot be used for titration because the nitrites destroyed thereupon react with the phenylanthranilic acid.

SUMMARY

1. The Kuznetsov-Budanova method for the determination of manganese in ferrous and non-ferrous metals by means of a persulfate-cobalt catalyst has been checked.

2. It has been found that this method can completely replace the persulfate-silver method of determining manganese and can be recommended for wide practical application.

3. Using this method as a basis, another one has been developed for the simultaneous determination of manganese and chromium on one aliquot of steel or cast.

4. The method worked out is finding application in factory laboratories.

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HISTORY OF THE DEVELOPMENT OF ANALYTICAL CHEMISTRY IN RUSSIA.

A RATIONAL METHOD OF CHECKING THE COMPOSITION OF A COMPOUND FROM ANALYTICAL RESULTS PROPOSED BY P. EINBRODT

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About 100 years ago Pavel Einbrodt, the Professor of Chemistry at Kharkov State University, published an interesting paper [1], under the title " Concerning the arithmetic control of analysis and the formula deduced on the basis of the analysis'' . In this article he pointed out that in the usual method of comparing the percentage composition found with the calculated value, the difference between the experimental and theoretical amount of a given element leads to an error which is inversely proportional to the atomic weight of this element, since in the course of the subsequent determination of the number of atoms of this element in the formula, its percentage content is divided by the atomic weight.

He observed further that an error in the determination of one of the elements leads to a smaller error in the indirect determination of any other element in the same compound, the greater the number of atoms of this second element contained in the compound.

Einbrodt emphasized that these considerations have a special significance for the analytical control of the formulas of organic compounds.

In order to increase the accuracy of calculation he proposed that the content of each element be divided by the product of the number of its atoms and its atomic weight, and then to compare these coefficients with one another and with a "normal coefficient" which he calculated from the formula $Q_i = 100/M_i$, where M_i is the molecular weight corresponding to the i'th formula chosen for the given compound.

From this it is clear that the coefficient for each k'th element comprising the i'th formula of the given compound is determined by the expression:

$$q_{ik} = \frac{100W_k}{n_{ik}A_k} \qquad (1)$$

where W_k- is the amount of the k'th element determined experimentally in 1 g of material: n_{ik} the number of atoms of the k'th element in the analytically checked i'th formula; A_k- the atomic weight of the k'th element.

Einbrodt affirmed that "if both formula and analysis are correct, then all the coefficients should be the same'', i. e. each of the values of q_{ik} should coincide with the normal coefficient Q_i. This statement is correct since from the very definition of the value of W_k it is obvious that

$$W_k = \frac{n_{ik}A_k}{\sum\limits_{k=1}^{p} n_{ik}A_k} = \frac{n_{ik}A_k}{M_i}, \qquad (2)$$

where p- is the number of all the elements making up the given compound.

On the other hand, as Einbrodt writes, "any error in the correct formula - in the determination of the amount of an element, or in the formula derived - as the result of a correct analysis should appear as differences in the coefficients obtained (q_{ik}) both among themselves and also with respect to the normal coefficient Q_i".

Einbrodt applied his method for checking the formulas of chloroacetic acid and meconic acid suggested by Dumas, Lowig, and Liebig. From the tables adduced in his work it is obvious that all these formulas should be rejected because the coefficients found differ among themselves fairly considerably. Einbrodt, however, refrained from drawing a categorical conclusion and endeavored to justify the discrepancies found on the basis of analytical errors and the purity of the materials. Einbrodt did not pay attention to the fact that his method could be used so as to correct the formula if it had been chosen incorrectly, so that the molecular weight of the test material could be evaluated.

Einbrodt's contemporaries were unable to use or appreciate his method since only a very few of the formulas in use at that time, as listed in Berzelius's book [2] were correct. Up to the time when Butlerov's structural theory appeared, Einbrodt's method, which anticipated his contemporaries' potentialities, was finally forgotten, and as a result chemists who establish the formula of compounds from analytical results, even now use methods which Einbrodt correctly criticized 100 years ago

It is clear to us that Soviet chemists should turn their attention to Einbrodt's forgotten method and use it widely in their work. Below we have given some examples of the calculations involved in Einbrodt's method so as to illustrate its possibilities. In these examples we used the more convenient coefficients $M_i/M_i = 1$ for each compound instead of Einbrodt's normal coefficient which is equal to $100/M_i$. The calculations themselves are, where necessary, supplemented by mathematical statistical methods, which enhance the value of Einbrodt's method even more.

As our first example we have considered the choice of formula for papaverine which as is known [3], was not established immediately, since the formula accepted nowadays viz. $C_{20}H_{21}O_4N$ and which was proposed as long ago as 1848 by Merck was regarded as incorrect for a long time, and the formula $C_{21}H_{21}O_4N$ was put forward in its place by Hess in 1870.

Let us assume that as a result of one combustion it was established that papaverine contains C-70.90% and H-6.21%, while analysis for nitrogen gave N-4.16%. In this case the oxygen content by difference will be 18.73%. In Table 1 these results are initially used for calculating the coefficients q_{ik} corresponding to Hess' formula. It is clear from Table 1 that the coefficient for carbon differs appreciably from all the other remaining values of q_{ik} which are considerably greater than unity. A normal comparison of the mean of the three q_{ik}'s which are greater than unity, with the value 0.988 [4], shows that the differences between them cannot be explained by random errors, since the probability of a value $t_1 = 10.2$ as a result of random errors for a number of degrees of freedom $k = 2$ is less than 0.027 [5]. In so far as all the values of q_{ik} differ from unity by more than 1%, it is obvious that this deviation is connected with an incorrect choice of formula, since the determinations of individual elements in elemental analysis can scarcely include errors of more than 0.5%. Further comparison of the values of q_{ik} shows that the values of q for H, N, and O are practically the same; from which it follows that the indices for the symbols H, O, and N in the formula $C_{21}H_{21}O_4N$ are correct, while the index for C contains an error, with a consequent error in the molecular weight.

In order to find the correct value of the molecular weight M_x formula (3) can be used

$$M_x' = \frac{n_{ik}A_k}{W_k}, \tag{3}$$

which is easily derived from formula (2), if 100 is put instead of M_i and it is taken into account that $q_{ik} = 1$ for such a substitution. It was in this way that the values of M_x adduced in Table 1 were derived; the mean value of $\overline{M}_x = 339.7$ is less than the molecular weight corresponding to Hess' formula by 11.7, i.e., by an amount approximately equal to the atomic weight of carbon. This confirms the correctness of the formula $C_{20}H_{21}O_4N$, as is also proved by the values of q_{ik} given in the last column of Table 1.

Table 1

Application of Einbrodt's method for choosing the formula of papaverine

			Hess' formula $C_{21}H_{21}O_4N$ $M = 351.4$				Merck's formula $C_{20}H_{21}O_4N$ $M = 339.4$	
	W_k	A_k	n_{ik}	q_{ik}	$q_{ik} > 1$	M_x	n_{ik}	q_{ik}
C	0.7090	12.010	21	0.988	—	—	20	1.002
H	0.0621	1.008	21	1.032	1.032	340.7	21	0.996
N	0.0416	14.008	1	1.044	1.044	336.7	1	1.008
O	0.1873	16.000	4	1.029	1.029	341.7	4	0.993
		Mean		1.023	1.035	339.7		0.9998

$$s^2 = 4.2\cdot10^{-5};\ s = 4.6\cdot10^{-3};\ t = \frac{1.035 \quad 0.988}{4.6\cdot10^{-3}} =$$

$$=10.2;\ P(|t| > 10.2) < 0.027;\ 351.4 - \overline{M}_x = 11.7 \sim 12$$

Table 2

Application of Einbrodt's method for choosing the formula of bromphenolblue

			$C_{19}H_{12}O_6Br_4S$ $M = 688.0$				$C_{19}H_{10}O_5Br_4S$ $M = 670.0$	
	W_k	A	n_{ik}	q_{ik}	$q_{ik} > 1$	M_x	n_{ik}	q_{ik}
Br	0.4775	79.916	4	1.028	1.028	669.5	4	1.001
S	0.0476	32.06	1	1.022	1.025	673.5	1	0.995
		Mean		1.025		671.5		0.998

$$688.0 - \overline{M}_x = 16.5 \sim 18$$

Normally, in order to determine the formula of a compound, analysis is confined to the determination of one or two elements. In those cases where the molecular weight of a compound is established by independent determinations, it is obvious that any n_{ik} can be calculated by means of equation (3). In those cases where the correct value of M is unknown, one must resort to the methods shown in Table 1. As an example we shall consider Orndorff and Sherwood's analysis [6], on the basis of which they concluded that bromophenolblue is a sulfonphthalein and not a sulfonic acid. Results for bromine and sulfur, which were found to be 47.75 and 4.76, respectively, were used in Table 2. From this table it is clear that the values of q_{ik} correspond to the formula of a sulfonic acid and are approximately equal, but are greater than 1 by more than 2%; such a deviation cannot be explained by random errors. The values of M_x, calculated by means of formula (3) are very near to the molecular weight corresponding to a sulfonphthalein. The values of q_{ik} correspond to the formula $C_{19}H_{10}O_5Br_4S$ and are very nearly one.

These examples are enough to recommend Einbrodt's method for wider application.

SUMMARY

1. A rational method which was proposed 100 years ago by P. Einbrodt, Professor of Chemistry at Kharkov University, for checking th composition of a compound from analytical results has been described.
2. Examples are given of the application of this method under present day conditions.

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1) See Consultants Bureau Translation, page 361.

IVAN PAVLOVICH ALIMARIN

(On the occasion of his fiftieth birthday)

In August, 1953, Professor Ivan Pavlovich Alimarin, one of the foremost analytical chemists of our country and a doctor of chemical sciences celebrated his fiftieth birthday and 30 years of scientific and teaching activity.

All his many-sided activities have been devoted by Alimarin to scientific-teaching and scientific-organization work connected with the development of analytical chemistry in Russia.

Alimarin, while still a youngster of 16, on the advice of his teacher, Prof. K. I. Viskonta, started to work at the Plekhanov Institute of National Economy in the Student's faculty on practical inorganic chemistry. He devoted all his spare time enthusiastically to experiments in analytical chemistry.

In 1928 Alimarin started to work as an assistant in the Mineralogical section of Moscow State University, from which he proceeded to the M. V. Lomonosov Institute of Fine Chemical Technology as a lecturer, and, ultimately, from 1948-1953 was professor at the head of the analytical chemistry section.

Since April 1953 he has been the head of the chair of analytical chemistry in Moscow State University.

A new stage in Alimarin's life was reached when he started to work (1923) in the Institute of Applied Mineralogy (at present VIMS). In this institute, where he worked for 30 years, he personally carried out hundreds of complex analyses of mineral raw materials and developed new analytical methods. Initially he worked as a scientific coworker, but subsequently became head of the analytical laboratory, and in this work he became an outstanding analytical chemist. From 1949 he headed the laboratory of Microchemistry in the V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry.

In the course of more than 30 years, Alimarin combined both scientific and teaching activity, and his fruitful activity shows him to be one of the foremost specialists in the field of analytical chemistry.

His scientific activity is distinguished by its wide variety; either on his own or in conjunction with other workers he has carried out about 200 researches. The basis of all this work was indissolubly related to the problems of improving the national economy.

The field in which he may be regarded to have specialized in mainly is that of analysis of small amounts of material.

He studied the distribution of rare elements in minerals, as a result of which he has produced new analytical methods. He also carried out work on the chemical concentration of the rare elements. As a result of this work, which extended over the course of many years, he proposed new methods of concentrating and quantitatively determining the following elements: Nb, Ta, Zr, V Ge, Re, In, Te, Ga, Li, etc.

Of particular interest are the methods of isolating and determining Nb, Ta, and Ge, which find manifold uses in Russian laboratories.

The most recent investigations of Alimarin and his coworkers have been along the lines of developing new physico-chemical methods (colorimetry, polarography, amperometry), for scattered elements. New methods have been developed or old ones improved; colorimetric determination of V, Nb, Te, Cr, Si, polarographic determination of Sn, Ge, Cr, V and an amperometric titration of Fe, Cr, V.

He has also adopted the methods of micro- and ultra-micro- methods of analysis, a logical development, since he has always been interested in the chemistry of small amounts.

Alimarin has also developed special methods and apparatus for use in geological prospecting which have found wide application.

As a result of his work along these lines, a technique of microanalysis of silicate minerals and ores has been perfected. Moreover, in conjunction with B. Frid he has written a monograph on "A practical textbook on the microanalysis of minerals and ores".

A second edition of "Qualitative Semi-microanalysis" by I. P. Alimarin and V. N. Arkhangelskaya, which has been successfully used in University courses in qualitative analysis, has recently come out.

In search of new and better analytical methods, Alimarin has done a lot of theoretical work on the study of the mechanisms of analytical reactions, which occur during the formation of precipitates and complex compounds. The study of the structure of precipitates formed during analysis, of the complex compounds of niobium and tantalum, and of the reactions of several of the rare elements in lower oxidation states belong to this category.

Alimarin has widely used the periodic law of Mendeleev in his work. Using this law during a study of analogous analytical properties of the elements in relation to their position in the periodic system, he has worked out the following new, original reactions: the formation of a heteropolyacid of germanium and its compound with orthohydroxyquinoline; the precipitation of niobium and tantalum with phenyl arsenic acid, the interaction of niobium with thiocyanic acid, thymol, guaiacol, and hydroxyanthraquinone.

Alimarin has devoted a lot of attention to the state of an element in solution (ions, molecules, colloidal particles) and to the step-wise process of reaction in solutions.

What has already been said does not by any means exhaust the work carried out by Alimarin.

In the course of many years his activity has been characterized by the fact that his most important researches and his newest achievements in the field of analytical chemistry have been reflected in his teaching work. It is his wish to communicate to his students his own experience and also the classical methods of analysis. At the same time he tries to inculcate in them a spirit of alertness and accuracy in their work. He pays a great deal of attention to the work of his students and to the theses of candidates for the doctor and master's degree, as well as a consultant to workers in factory laboratories.

His coworkers, and those working under his direction, value his work and successfully apply his experience in chemical analysis. Purposefulness, vigor, and a polished style of work are characteristic of Alimarin's students.

Alimarin participates fully in the various All-Union conferences on analytical chemistry, on the editorial board of State Chem. Press and in the J. Anal. Chem., and also in the chemical section of VAK.

For his work he has been rewarded by the Soviet Government.

In 1944 he was awarded the Order of the Red Star, and in 1953 was awarded the Order of Lenin.

In noting that today Alimarin celebrates both his fiftieth birthday and 30 years of scientific-teaching activity, his comrades, coworkers, and a wide circle of Soviet analytical chemists will send him their sincerest wishes for his health and for his fruitful work for the good of Russia.

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Rates for translation into English

Language	Rates [illegible]
French	[illegible]
German	10.00
Italian	[illegible]
Russian	[illegible]
Spanish	[illegible]
Dutch	[illegible]
Other languages	[illegible]

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New York [illegible]